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BUTTER

ITS ANALYSIS & ADULTERATIONS

HEHNER AND ANGELL

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BUTTER

ITS ANALYSIS AND ADULTERATIONS

SPECIALLY TREATING

ON THE

DETECTION AND DETERMINATION OF FOREIGN FATS

BY

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Second Edition, entirely Re-written, Improved, and Augmented

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PREFACE TO THE SECOND EDITION.

WHEN we published, in April, 1874, the first edition of this book, we were well aware that a process for the detection and determination of foreign fats in butter was urgently needed, and that any method, based upon sound principles, would be warmly welcomed.

We are happy to state that we were not disappointed in our expectations. One chemist after another critically and carefully examined our process, and it was soon adopted, with some modifications in its execution, in nearly every laboratory all over the country in which articles of food are examined. Butter analysis has, in fact, now been placed upon as sound a basis as any branch of food analysis, and the most difficult of problems is considered to be solved by every one who has a voice in this matter. A few persons have not been wanting, who from prejudice, or from other causes, have struggled against the adoption of our process, but they have, happily, been overruled.

The composition of butter-fat has been closely studied during the last few years, and many interesting facts, of which we give a short account in the following pages, have been brought to light. The subject is as yet by no means exhausted, but as far as the practical part is concerned, we feel confident that no great or important improvements of the process will be introduced for some time to come.

That this second edition is indeed an improved and augmented one will be evident from even a very cursory examination of its pages, there being but few lines which do not bear the marks of the revision. The chapter on the analysis of butter-fat is indeed entirely re-written, and brought up to the standing point we have attained through the labours of Mr. Bell, Dr. Dupré, Dr. Muter, and others. An entirely new chapter on the specific gravity of butter-fat has been added.

We trust that the book will, in its new form, be as favourably received by both analysts and the trade, as it was in its first issue. We hope that a real want is satisfied by it, it giving to the analyst accurate methods for detecting adulteration, tested carefully and found sound and correct, and protecting the trade from unjust prosecutions under the Sale of Food and Drugs Act, and from the dangers of the old methods of butter analysis.

LONDON AND SOUTHAMPTON,

April, 1877.

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BUTTER :

ITS ANALYSIS AND ADULTERATIONS.

CHAPTER I.

THE COMPOSITION OF BUTTER.

BUTTER consists of the fatty portion of the milk of the cow. It is suspended in the milk in the form of minute oil globules, which, on allowing the secretion to remain undisturbed for some hours, on account of their having a lower specific gravity than the liquid in which they float, rise to the surface and form a layer of cream.

It was for some time supposed that the fat globules in milk were prevented from coalescence by some kind of protecting membrane, presumedly albuminous, and this view appeared to be borne out by the fact, that the fat globules are not dissolved when the milk is agitated with ether, but only after desiccation will the milk yield up its fat to solvents. Recently, however, it has been shown that if the milk's solids be again taken up with water so as to re-form the milk, the same indifference to the action of solvents is observed. This proves that no true sac or pellicle can exist, but that the globular bodies are protected from immediate contact with the solvent by the presence of the surrounding medium.

Cream contains, besides large quantities of fat and water, notable proportions of casein and of sugar of milk. The relative amounts of these ingredients vary considerably, according to the time allowed for the separation of the cream, the temperature, the quality of the milk, and other circumstances, but genuine creams of good quality, such as have been analysed by Hassall with the subjoined results, yield not less than 30 per cent. of pure fat.

Samples 1-3 were purchased of milkmen, 4-6 being obtained direct from the dairy.

Water	...	62.12	61.50	63.24	49.10	43.04	45.82
Fat...	...	30.64	32.22	31.42	42.82	44.76	44.33
Casein	...	5.83	5.14	2.70	5.20	7.40	6.38
Sugar of milk		1.27	0.74	2.36	2.46	4.45	2.92
Ash...	...	0.14	0.40	0.28	0.42	0.35	0.50
		<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
		100.00	100.00	100.00	100.00	100.00	99.95

By violent agitation in a churn or any other suitable vessel the oil globules of the cream conglomerate for the most part, and uniting form a fatty mass, which invariably contains small quantities of the other constituents of the cream, which cannot be removed by mechanical means, if we except the small amount of sugar of milk which may be washed off. This mass, to which some salt is generally added during the process of preparation, is the butter of commerce.

Butter may vary much in colour and flavour, even when quite fresh and sweet, these qualities being governed by a great variety of circumstances. Thus the flavour of the food of the cow in many cases may be distinctly perceived in the fresh butter, while the colour ranges, according to season and food, from a rich to a very pale yellow.

Carefully prepared butter is homogeneous throughout its mass, pellucid in appearance, and free from superfluous water. It soon loses its sweet odour and taste, owing to the partial

decomposition of the fatty and the albuminous portion, this change being retarded by the addition of salt; hence butters are commercially distinguished as fresh and salt butters.

Its constituents are in all cases the same as those which enter into the composition of milk and cream, namely, fat, water, casein, sugar of milk, and mineral matters, consisting for the most part of alkaline phosphates. To these is to be added the salt used in its preparation and for its preservation. The proportion of sugar of milk, which in some cases is for the most part changed into lactic acid, is always very small, it never amounting to more than a few hundredths of a percentage. Hence it may in all cases be safely disregarded.

I. The Fat of Butter.—Butter-fat is a highly complex substance, including a greater variety of glycerides than any other fat known. It has long been regarded as a mechanical mixture of different glycerides, but the latest researches, which will be found in another chapter, go far to prove it to be not a mixture of tri-glycerides, but a mixed ether, a tri-glyceride containing different acid radicles.

The acids, which are said to occur in butter-fat, in combination with glycerin, are palmitic, stearic, and oleic, butyric, caproic, caprylic, and capric. Besides these (the occurrence of at least one of which is doubtful), there have been alleged to be present margaric and butyroleic acids, which, however, are now no longer recognised as distinct compounds naturally occurring.

As a great part of the methods of butter analysis detailed in this book cannot be properly understood without a knowledge of the properties of the acids enumerated and of their tri-glycerides, we shortly append their physical and chemical characteristics.

Palmitin, $C_{51}H_{98}O_6$ or $C_3H_5(C_{16}H_{31}O_2)_3$ is a white solid substance, sparingly soluble in cold, far more so in hot

alcohol, from which it crystallises on cooling in shining laminae, having a silky appearance when dry. It very readily dissolves in ether. It has, like most other solid triglycerides, three different melting points, 46°C ., 61.7° , and 62.8° (Duffy). It solidifies at 45.5°C .

Palmitin occurs abundantly in many solid natural fats, animal or vegetable, especially in palm oil, and in Chinese tallow. The solid part of butter-fat appears for the most part, if not entirely, to consist of tri-palmitin or a substitution product, which yields palmitic acid and butyric acid on decomposition.

Palmitic acid, $\text{C}_{16}\text{H}_{32}\text{O}_2$ closely resembles in its physical appearance the corresponding tri-glyceride. It is a white solid, quite insoluble in water, than which it has a lower specific gravity, is abundantly soluble in alcohol, especially when hot, and in ether. It melts at 62°C . 100 parts of palmitin yield 95.28 parts of palmitic acid.

Stearin, $\text{C}_{57}\text{H}_{110}\text{O}_6$ or $\text{C}_3\text{H}_5 (\text{C}_{18}\text{H}_{35}\text{O}_2)_3$ crystallises in white, silky laminae and needles. It is nearly insoluble in cold, but easily so in boiling alcohol. It dissolves freely in boiling ether, but on cooling it separates, only 0.4 in 100 parts of the liquid remaining in solution. The solubility in alcohol or ether is, however, much altered in the presence of olein and other glycerides.

It melts at 51.7° , 64.2° , and 69.7° in its three distinct modifications, in which also it exhibits widely different specific gravities, namely, 0.9867, 1.0101, and 1.0179 respectively, at 15°C .

The presence of tri-stearin in butter-fat is doubtful. Thus the substance, which Chevreul obtained from butter, and which he regarded as stearin, had a far lower melting point than pure stearin. We were not able to obtain any magnesium salt, on fractional precipitation, which had the composition of stearate of magnesia.

Stearic acid, $C_{18}H_{36}O_2$ crystallises in laminae or needles. It is quite insoluble in water, but soluble in alcohol and ether, and other solvents. It melts at $69.2^\circ C.$, or according to some at $75^\circ C.$ 100 parts of stearin yield 95.73 per cent. of stearic acid.

Stearin is the chief constituent of the harder animal fats, such as beef and mutton suet, but it has been found in nearly every natural fat examined in which the acid sometimes occurs in the free state.

Olein, $C_{57}H_{104}O_6$ or $C_3H_5 (C_{18}H_{33}O_2)_3$. The liquid portion of all hard animal and vegetable fats, and of the non-drying oils, consists of tri-olein. When quite pure it is a colourless liquid, without smell or taste, easily soluble in alcohol and ether, but insoluble in water. Strong nitric acid converts it into an isomeric solid substance, *elaëdin*.

Olein yields 95.70 per cent. of oleic acid. *Oleic acid*, $C_{18}H_{34}O_2$ is a neutral oily liquid, without colour, smell, or taste, insoluble in water, very easily dissolved by alcohol, and by all proportions of ether. It crystallises from its alcoholic solution in the form of white needles, which fuse at $14^\circ C.$, and again become solid at $4^\circ C.$

Oleic acid is a good solvent for stearic, palmitic, and other acids, the mixtures having a lower melting point than that calculated; the same may be said of mixtures of the corresponding tri-glycerides.

Oleic acid, when heated with solid caustic alkalies, is converted into palmitate and acetate with evolution of hydrogen.

Butyrin, $C_{15}H_{26}O_6$ or $C_3H_5 (C_4H_7O_2)_3$ is an oily liquid possessing a rancid odour and an acid taste. It is heavier than water, and insoluble in that liquid, but easily soluble in alcohol or ether.

Butyric acid, $C_4H_8O_2$ the most interesting constituent

of butter-fat was discovered in that substance by Chevreul. It has since been obtained from a great variety of sources; thus it was found in the locust bean, in the fruits of the soap tree, and of *Gingko biloba*, in sour gherkins, in the sauerkraut of the Germans, in human perspiration, in flesh, in oil of amber, and in cod-liver oil. It occurs in small quantities in some mineral springs, and is formed by the fermentation of sugar, starch, and lactic acid, it thus being usually prepared. It is not found in any animal fat except in butter and cod-liver oil.

Butyric acid is a colourless liquid, strongly acid, and possessing an odour as of acetic acid and of butter combined. Its taste is sour and rancid in the highest degree. It boils at 157°C. , and is soluble in water, alcohol, and ether. It may be volatilised and distilled without change or decomposition.

Caproic acid, $\text{C}_6\text{H}_{12}\text{O}_2$ was first found in butter. It also exists in cheese and in cocoa-nut oil. It is a clear and colourless liquid, sparingly soluble in water, but easily dissolved by alcohol. It boils at 202°C. , and possesses a specific gravity of 0.922.

Caprylic acid, $\text{C}_8\text{H}_{16}\text{O}_2$ resembles in its physical characters the preceding, with which it is usually found associated. It has but a feeble odour, solidifies at 12°C. , boils at 236°C. , and is slightly soluble in water, 126 parts of which at 10°C. and 50 parts at 100°C. dissolve one part of the acid. It is quite insoluble in alcohol and ether, and has a specific gravity of 0.911.

Capric acid, $\text{C}_{10}\text{H}_{20}\text{O}_2$ has been found in butter, cocoa-nut oil, and in fusel oil. It is a white solid crystalline body, melting at 29.5°C. , easily soluble in alcohol and ether, but dissolved only with great difficulty in large quantities of boiling water. It is not volatile to any considerable degree.

The four acids last described were all discovered in butter-

fat. They are distinguished from the first three, namely—palmitic, stearic, and oleic acid, by being more or less soluble in water, and volatile without decomposition. We may therefore comprise them under the term “soluble” or “volatile” acids, while the others may be called the “insoluble” fatty acids.

The latter amount to about 87·5 per cent., the former to from 6 to 7 per cent. of the butter-fat, butyric acid being the by far predominating representative of the soluble acids.

As far as we are aware, but one analysis of butter-fat has been published, which one, moreover, is very unsatisfactory, and has been proved to be positively erroneous. It is by Bromeis, and quoted by Fremy and Pelouze in their “*Traité de Chimie.*”

Margarin	68
Butyrolein	30
Butyrin, caprin, and caproin	2
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The margaric acid of Bromeis has been proved by later investigators to consist of stearic acid, associated with volatile acids; and this circumstance explains why Bromeis so greatly underrated the quantity of volatile acids. At the same time, it has never been proved to satisfaction that there is any difference between the oleic acid of butter and that of other fats. “It appears from the experiments of Gottlieb, that it is really identical with oleic acid, and exhibits the characters observed by Bromeis only after it has been considerably altered by exposure to the air.” (Watts’ Dictionary.) It will be conclusively shown, in a subsequent chapter, that the quantity of volatile acids is much more considerable than the analysis above quoted would lead one to believe.

There are no methods for quantitatively separating stearic from palmitic or even from oleic acid, and all analyses dealing with these bodies separately can only be approximative.

II. Water.—The most variable constituent of butter is the water which it unavoidably contains ; according to the care which has been employed in the process of manufacture, smaller or larger quantities are incorporated with the butter, the perfect removal of which by mechanical means is practically impossible.

As an absolutely valueless and negative constituent, it should be squeezed out as completely as possible during the preparation of the butter. The buyer and consumer merely intends to purchase the fat, and should not therefore be served with perhaps one-fifth of the total weight of his purchase of water, paying the same price for it as for butter. Good butter, carefully prepared and repeatedly pressed directly after being taken out of the churn, does not contain more than 12 per cent., and can easily be made with less than 10 per cent. Any considerable excess should therefore be treated as an adulteration, or, at least, as evidence of culpable carelessness on the part of the manufacturer.

Butter supplies to most people the largest amount of fat they take into their systems. Dr. Parkes estimates "that most persons take from $1\frac{1}{2}$ to 2 oz. daily ;" so that it is a matter of great importance to every individual to get pure butter, and not, as often happens, 15 or 20 per cent. of water. Parkes and Calvert fix the normal amount of water at from 5 to 10 per cent. ; Hassall and Wanklyn at 12 per cent. ; Watts gives 1 per cent., which appears to be a misprint. Our experience has led us to agree with Hassall and Wanklyn in fixing 12 per cent. as the maximum limit of the amount of water. Very frequently, however, a much larger percentage of water is met with (see tables, pages 15 and 19) ; thus Hassall found that the amount of water ranged in salt butters

from 8·4 to 28·6 per cent., and in fresh butter from 4·18 to 15·43 per cent. Wanklyn gives in fifty samples of the butter supplied to the London workhouses in 1871, the water ranging from 8·6 to 23·7 per cent. We have met, in one case, with the extraordinary amount of 42·3 per cent. Bell found the water to fluctuate between 4·15 and 20·75 per cent.

Several methods may be adopted in order to produce an excessively aqueous butter—either the milk is purposely left in undue proportion during the process of manufacture, or it is afterwards added by stirring the fused butter with water, and cooling the mixture very rapidly; or lastly, the butter and the water may be triturated together in the cold. Thus, however, a product is obtained which is very light in colour and texture, enclosing a great number of air bubbles, which at once characterise the mixture as adulterated.

An unusually low percentage of water is likewise a suspicious circumstance. If a butter containing the normal amount of water be mixed with foreign fats containing no water, a diminution of moisture will be the natural result. Thus we have met with a sample, undoubtedly adulterated, containing but 3·83 per cent., and we are by no means sure that the low percentages of water found by several of the observers above quoted, are not likewise due to the fact that the butter was mixed with foreign fat. At the time the analyses referred to, however, no method for detecting admixture of foreign fats with butter was known.

III. Casein, or Curd, is the nitrogenous matter of the milk, some of which is invariably skimmed off with the cream either in the coagulated state, or in solution, and thence finds its way into the butter. Taking the average of our analyses quoted in Chapter II., we find that butter contains about 2·2 per cent., ranging from 1·1 to 5·1 per cent. Hassall and Parkes give from 3 to 5 per cent. Casein, however, may be mixed with butter in much larger quantities, so

as to give rise to the so-called cheesiness. The less casein a butter contains the better, since this substance, like all other albuminous matters, is apt to decompose—to induce decomposition of the bodies with which it may come into contact, and to hasten that splitting-up which takes place in pure butter when exposed to the air. The keeping properties of a butter are therefore dependent, in some measure, upon the amount of casein present. An excess of casein renders necessary an excess of salt to counteract the pernicious influence of the nitrogenous matter; consequently a careless or fraudulent manufacturer gets the benefit of the increase of weight by both substances.

IV. Salt.—Our experience teaches us that butter contains on an average 2·5 per cent. of salt. Butter is spoken of as either fresh or salt butter. This distinction is convenient for commercial purposes, but would be a useless introduction in this book, as no defined line can be drawn between the two; to each salt has been added, whether it be a so-called fresh or salt butter.

Hassall found the salt, in one instance, as high as 28·6 per cent. Wanklyn's fifty analyses give a range of from 0·1 to 10·7 per cent. We think that the amount of salt in any butter should never exceed 8 per cent. An excess of salt is commonly accompanied by an excess of water, and frequently by an excess of curd; it would not be practical to use salt alone as an adulterant, since it is so easily detected by the taste, and therefore reduces the commercial value to a greater extent than it increases the weight of the butter.

To sum up. The amount of water in butter should not be higher than 12 per cent., the curd and the salt should be about 2·5 per cent., the latter may rise as high as 8 per cent. The fat, which averages at about 87 or 85 per cent., should not fall in any case below 80 per cent.

CHAPTER II.

ON THE DETERMINATION OF THE CONSTITUENTS OF BUTTER.

THE substances with which we have to deal in this chapter are water, casein, salt, and fat; the analysis of the latter being by far the most important point in butter examination, will be specially treated with in another chapter.

For the determination of the water, two processes may be employed. The first and older method is frequently recommended, but, as may be seen, is only capable of giving approximate results, and more fit for the butter-dealer than for the chemist. It consists in fusing the butter in a graduated tube, about half an inch in diameter, and similar to those used for the estimation of cream in milk. The butter-fat separates in consequence of its low specific gravity, the water, salt, and curd sinking to the bottom, and the amount of water being read off on the graduated scale. It is evident that this method is better adapted for the estimation of the fat than of the water.

The other method, the only reliable and accurate one, consists in drying a weighed quantity of butter in a porcelain or platinum dish, till all moisture is driven off. The drying may be done either on the water-bath, in the air, or on the sand-bath. If on the water-bath, the dish should not be too

small, as it is necessary frequently to shake the melted butter so as to facilitate evaporation of the water which collects below the fat. If the dish be too small and deep, the water does not evaporate at all.

If the drying be done in the air-bath, or upon sand, as has been recommended by Dr. Muter, the temperature should not exceed 110° or 115° C. This plan is by far preferable, on account of its rapidity and completeness.

A quantity of about three or four grammes is sufficient, provided the sample be cut from the middle of the mass submitted for analysis. To take more only adds to the trouble, and renders the process of drying clumsy, without materially improving the result. It must be admitted that not only water is volatilised during drying, but also any free volatile acid which may be present; but as the quantity of free acid in even highly rancid butters is but exceedingly small, this source of error may quite safely be disregarded.

The butter thus freed from water is weighed, and the percentage of loss calculated. The fat is then again fused, and dissolved in about 10 c.c. of ether. The ethereal solution of fat is poured off, if the liquid be clear, into a weighed beaker, or, if necessary, filtered through a weighed filter. The curd and salt thus obtained are repeatedly washed with ether, until a drop of the filtrate evaporated upon a glass slide no longer leaves a greasy spot. The perfect removal of the fat is not very easy, and a comparatively large quantity of ether has to be used. The filter is dried in the water-bath, and weighed between two watch-glasses, so as to prevent any absorption of moisture from the atmosphere, the increase of weight, added to the weight of the residue in the basin, being calculated as curd and salt.

In order to save trouble, filters, instead of being weighed, are often counterbalanced by placing another filter of apparently the same size and weight upon the opposite pan of the

scales. This method is utterly unreliable, unless the filter be specially clipped with the scissors to the correct weight. Some filters stamped out from the finest Swedish paper differ very considerably, sometimes as much as 0.05 gramme.

The residue is now burned in the weighed basin to a white ash, which consists, in genuine butters, practically of salt only, and is accordingly calculated as such. The difference between the weight of the ash and that of the dry solids not fat, gives the amount of casein. If an accurate determination of the salt in the mineral residue obtained be deemed desirable, the chlorine must be determined by the usual nitrate of silver method, either volumetrically or gravimetrically, as circumstances may require.

The fat may be estimated either directly or by difference. The ethereal solution obtained may be evaporated in a small weighed flask or beaker; the ether may easily be saved by connecting the flask with a condenser. We can recommend a simple and effectual one, easily made by bending a narrow glass-tube into a V shape, each arm being a foot long. The bent tube is immersed in cold water, and the ethereal solution heated to boiling by means of a water-bath. When nearly dry, the flask containing the butter fat is placed into the steam-bath, and dried till a constant weight is obtained. The indirect determination is much the quickest, and capable of yielding very accurate results.

In lieu of ether, petroleum spirit or benzoline, recently distilled, may with advantage and considerable saving be employed.

According to the plan of analysis described in this chapter, a great number of determinations were made by us, some of which are appended to illustrate the composition of the butters of commerce :—

Water	9.7	10.1	13.0	11.2
Curd	3.5	2.8	2.7	3.1
Salt	2.1	0.7	0.4	2.0
Fat	84.7	86.4	83.9	83.7
			<hr/>	<hr/>	<hr/>	<hr/>
			100.0	100.0	100.0	100.0
Water	6.5	10.5	9.3	9.2
Curd	2.4	2.5	5.1	2.9
Salt	1.6	8.5	2.9	3.2
Fat	89.5	78.5	82.7	84.7
			<hr/>	<hr/>	<hr/>	<hr/>
			100.0	100.0	100.0	100.0
Water	7.7	8.6	6.4	8.6
Curd	1.9	2.8	1.6	2.0
Salt	2.0	3.1	1.8	2.1
Fat	88.4	85.5	90.2	87.3
			<hr/>	<hr/>	<hr/>	<hr/>
			100.0	100.0	100.0	100.0
Water	11.8	11.0	13.8	10.3
Curd	1.2	2.1	1.5	1.9
Salt	8.0	4.5	8.3	2.7
Fat	79.0	82.4	76.4	85.1
			<hr/>	<hr/>	<hr/>	<hr/>
			100.0	100.0	100.0	100.0
Water	11.5	9.7	7.9	9.1
Curd	2.3	1.2	1.6	2.0
Salt	3.4	4.9	3.9	2.6
Fat	82.8	84.2	86.6	86.3
			<hr/>	<hr/>	<hr/>	<hr/>
			100.0	100.0	100.0	100.0

Water	10·1	10·8	14·1	14·3
Curd	1·4	1·1	1·3	2·2
Salt	5·2	2·6	2·7	0·8
Fat	83·3	85·5	81·9	82·7
			<hr/>	<hr/>	<hr/>	<hr/>
			100·0	100·0	100·0	100·0

Water	12·4	9·5	11·5	11·4
Curd	1·5	1·3	2·8	2·4
Salt	1·0	2·2	1·6	2·5
Fat	85·1	87·0	84·1	83·7
			<hr/>	<hr/>	<hr/>	<hr/>
			100·0	100·0	100·0	100·0

Water	11·2	16·0	
Curd	1·9	2·4	
Salt	1·4	4·1	
Fat	85·5	77·5	
			<hr/>	<hr/>	
			100·0	100·0	

Several very exceptional samples have come under our notice :—

Water	3·8	24·0	42·3
Curd	3·3	6·9	7·8
Salt	6·6	1·5	2·7
Fat	86·3	67·6	47·2
			<hr/>	<hr/>	<hr/>
			100·0	100·0	100·0

CHAPTER III.

ON THE MICROSCOPIC EXAMINATION OF BUTTER.

MUCH has been said and written about the use of the microscope in connection with the detection of adulteration in food. By some chemists, pure and simple, this instrument has, until very recently, been viewed with distrust and jealousy ; on the other hand, microscopists are apt to rush into an opposite, and even more dangerous extreme, when their opinions are based solely upon a glance through the magic tubes.

It has been declared that a microscopic examination with polarised light is a reliable means of distinguishing pure butter from that which contains an admixture of less palatable fats ; this, we are of opinion, is saying too much for the microscopic diagnosis of butter.

In butter analysis it is dangerous to rely too implicitly upon microscopic appearances ; the microscope, however, should not be entirely dispensed with, it frequently affording valuable corroborative evidence.

In no case does any fat in the raw state show crystals ; on the contrary, when a fat is fused the membrane is broken up, and all the constituents are melted into an oily liquid from which, on cooling slowly, the stearin and palmitin crystallize out. Beef, mutton, and pork fats show large cells of adipose

tissue, the contents of which depolarise light in an irregular manner.

Pure butter, freshly made, has no effect upon polarised light, except when it has been heated and allowed to cool again; when cooled very rapidly no perfect crystals are formed.

One part of ox fat and two parts of butter fat melted and poured into cold water, exhibited no traces of crystals, but contained much water, which might have been expelled by pressure.

If, therefore, upon crushing a small portion of the sample into a thin layer, and viewing it by polarized light, it shows stellate masses of crystals, it is a proof that some part of the fat has been melted down; and if no definite crystalline forms can be made out, but some portion or the whole of the mass possess any power over the polarised ray, it is probable that an animal fat has been added whilst in a state of fusion, and that the mixture was rapidly cooled.

It must not be forgotten that it is quite possible that in the summer time the outside portion of a pure butter may have fused and become crystalline. If some of a fat containing crystals be placed upon a slide, and a drop of castor or olive oil be applied, and pressed out with a thin glass cover, the depolarisation of light is much enhanced. A revolving black cross, not unlike that on some starch grains, is seen in great perfection. These crosses are most clearly defined in the crystals obtained from butter, and these thus mounted form a brilliant polariscope object for a one-third lens. The oil, however, exerts a solving action upon the crystals, and they soon disappear.

Thus far and no farther, as it seems to us, can the microscope assist us in this matter, but even such indications are valuable, especially when subsequent analysis proves the sample to be an adulterated article, the microscopic evidence

in such a case frequently helps to clench together the whole superstructure, and thus certainty is made doubly sure.

It has been asserted, with astonishing pertinacity, that the globules composing the fat in milk may distinctly be seen by the aid of the microscope in genuine butters, while "crystalline arborisations noticeable among the globules of fat will give undeniable testimony to the proportion of foreign ingredients fraudulently introduced." Now, the truth is, that the oil globules of the milk are broken up and beaten into a mass during the process of churning. Some few globules may escape destruction, but to found upon their number or their absence a test for the genuineness of butter is utterly absurd. Crystals are merely an indication that fusion has taken place, whether of the butter or of any added fat.

It must also be remembered, that in some butter-making districts, particularly in Devonshire, it is a common practice to scald the cream before churning it into butter, and in cold weather the temperature of the churn is raised by rinsing it out with boiling water. These proceedings would, in most cases, give rise to a crystalline appearance of the resulting butter.

The microscope is, however, capable of furnishing evidence of other adulterations of butter, which sometimes, though rarely, occur. Thus starch, ground or mashed potatoes, have been known to be used as adulterants, especially on the Continent, the presence of which would at once become evident by microscopical examination. Animal membrane, adipose cells derived from dripping, vegetable fibres introduced by foreign ingredients, would point out the presence of adulterating substances; they have all from time to time been met with. The relations existing between the microscopic appearance, and the results obtained by chemical analysis, may be seen in several cases by reference to table, page 19.

In this table we give the figures obtained in nineteen analyses of butters which had undoubtedly been manipulated; in some cases water only was added, in others foreign fat, and in some both water and foreign fat. In most of these cases there is no doubt that fusion formed a part of the method adopted.

No.	Water per cent.	Salt per cent.	Curd per cent.	Insol. fatty acids per cent.	Microscopic appearance.
1	15.6	8.5	0.41	89.33	Crystalline.
2	16.2	2.9	2.57	93.87	Very crystalline.
3	16.5	6.9	1.1	89.9	Sphaeroid crystals
4	22.19	5.68	1.02	87.51	" "
5	20.94	5.6	1.8	89.45	" "
6	6.6	2.6	5.08	92.2	" "
7	8.9	8.4	1.2	93.2	" "
8	13.68	2.2	2.79	93.3	" "
9	13.1	3.5	3.4	86.6	Crystalline.
10	9.95	4.08	3.8	92.53	Very crystalline.
11	13.90	2.91	2.32	91.9	" "
12	19.6	8.0	1.96	87.4	" "
13	4.08	2.33	7.39	91.79	" "
14	12.0	2.9	1.29	92.1	Many small crystals.
15	5.9	3.7	2.7	91.9	Crystalline.
16	6.9	3.85	2.5	93.3	{ No distinct crystals, whole mass de- polarised light.
17	11.67	3.22	1.31	91.04	
18	5.1	1.5	*2.9	93.9	Sphaeroid crystals.
19	16.9	9.2	1.29	88.0	Not recorded.
					Crystalline.

Nos. 4, 9, 12, and 19 are the only crystalline butters which

* This was not true casein, but an artificial substance of vegetable origin, made to represent the curd.

gave a normal percentage of insoluble acids, and in three of these the water was excessive.

In No. 16 was probably no butter at all. It had not been fused, or if so it had been rapidly cooled down, consequently it showed no distinct crystals, but the whole field was lighted up, much as it would be with raw mutton or beef fat.

CHAPTER IV.

THE FUSING POINT.

THE very gradual and almost imperceptible manner in which fats, particularly butter, begin to soften, melt, and liquefy on the application of heat, renders it difficult to fix the point of actual fusion.

We employ the term "fusing point" with some reserve. Most fats, if not all, are mixtures of different glycerides, amongst which olein is rarely absent. This glyceride, possessing the power of dissolving considerable quantities of palmitin or stearin even at ordinary, and doubtless far larger amounts at elevated, temperatures, plays the same part in soft fats as does water in saline solutions. It takes up on heating the glycerides which are mixed with it, and as soon as the mass is clear, it is termed "fused," although, properly speaking, it ought to be called a perfect solution. Hence it is obvious that the so-called fusing point is not a sharp, decided phenomenon.

Experience has taught all those who have worked upon butter analysis, that the fusing point—to take which so many methods have been devised—is, after all, of little value in affording an indication as to the genuineness or otherwise of a given sample of butter. Mixtures of solid and liquid fats can very easily be prepared, having the normal melting point

of butter without containing a particle of that substance. As the manufacturers of adulterated articles become educated and conversant with analytical methods, they employ the thermometer in the preparation of spurious butter, as the milk dealers are known to employ the lactometer or even chemical tests in the mixing of the watery liquids called milk. The melting point, taken alone, is therefore valueless; it assumes importance only when used as corroboration of the results obtained by other methods.

We think it well, however, to give the methods which have been devised, as the various plans proposed, intended more especially for determining the fusing point of butter, apply also to the other solid fats. We arrange the methods in the order in which they appear to have been published as near as this can conveniently be done.

The method adopted by Drs. Parkes and Campbell Brown was the first to bring the fusing point of butter at all under control. It was based upon the obscuration of the graduations of the thermometer by the gradually cooling fat, which was placed in a test-tube with the thermometer, and the whole immersed in water; heat being applied, two points, called respectively the "softening" and the "melting," were obtained. On cooling, the fat gradually obscures the readings, and thus three other points were obtained. They are shown in the following table, published in the *Chemical News* by Dr. C. Brown.

In this method the range of temperature given is extremely large, and the difference of 7° between the two first butters tabulated shows that the point of fusion is not well defined. We endeavoured to fix such a point, and to bring it more under control by the use of a little weight which, being placed upon the top of the fat to be fused, will sink when the fat is so far liquefied as to present less resistance than the weight can overcome.

	When heated.		On cooling.			Solid at
	Softens.	Melts.	Obscures reading.	Stem indistinct.	Stem invisible.	
	Degrees.	Degrees.	Degrees.	Degrees.	Degrees.	Degrees.
Butter from town-fed cows	20.5	24.4	28.3	24.4	22.8	16.7
Irish butter	23.9	31.7	22.7	21.7	20.5	16.7
" " best	20.5	26.6	25.5	23.3	21.6	18.9
" " low	24.4	31.7	27.7	25.0	23.3	20.5
Cornish butter	22.2	26.6	26.6	25.5	22.2	14.4
Canadian "	23.3	32.2	21.6	20.5	20.0	18.8
Kiel "	23.8	32.2	23.3	22.2	21.6	21.1
Suspected "	21.8	35.5	41.1	28.8	24.4	22.7
Lard	28.8	35.5	—	—	35.5	29.4
" "	26.1	30.5	26.6	26.1	24.4	20.0
" "	30.5	35.5	26.6	26.1	25.5	23.3
Palm oil	27.2	33.3	—	31.1	26.6	20.5
Butter with 20 per cent. of lard	27.7	35.5	30.0	27.7	24.4	21.6
Butter with 20 per cent. of tallow	31.1	37.2	26.1	25.0	24.4	22.7
Butter with 50 pr. cent. of dripping	27.7	33.8	33.3	27.2	23.8	21.6

The sinking point of the weight will nearly exactly coincide with the true fusing point, provided that the weight placed on the top is not too heavy in comparison to its bulk, as, for instance, a small piece of lead or brass would be. By making use of a glass bulb containing mercury, good results are obtained.

The bulb is made by blowing a small globe on the end of a piece of glass tubing of $\frac{1}{4}$ -inch outside diameter, and drawing it off with a tapering neck, very near the bulb. By this means a pear-shaped float is obtained, the size and shape of which is given in Fig. 1. Whilst the bulb is still warm, the open neck is dipped into mercury, and a small quantity allowed to run up into the bulb as the air contracts by cooling, in the same manner as thermometers are filled.



FIG. 1.

Sufficient mercury should be introduced to cause the bulb to weigh 3.4 grammes, which is the weight of the bulb used in our experiments. The bulb should displace as near as possible 1 c.c. of water when immersed in a burette, its specific gravity being therefore 3.4°. Absolute accuracy is not necessary, since it was found that a slight difference—say from 5 to 10 milligrammes—in weight, or a little variation in shape, does not materially affect the results.

By using such a weight, the sinking points of all butters come within the limits of three degrees, and any number of observers witnessing an experiment would agree when to read the thermometer. Beef, mutton, pork, and other fats are also equally constant, providing they are taken from the same part of the animal.

Further, in mixtures of foreign fats with butter, the sinking point varies in ratio to the percentage composition of the mixture, so much so, that in many instances the result arrived at by previous mathematical calculation practically coincides with the sinking point obtained.

Dripping or kitchen stuff, being often a mixture of different fats in unknown proportions, and having a sinking point very near that of butter itself, is an adulterant the presence of which the sinking point may give no indication; in this case recourse must be had to the estimation of fatty acids, which process will be spoken of further on. The reason why dripping has such a low sinking point is probably because it is composed of that part of the fat which is most easily fused in the process of cooking; in other words, it contains comparatively little stearin.

To take the sinking point of a butter, place 20 to 30 grammes of butter in a porcelain dish or glass beaker, and melt in the water-bath; when quite fluid, pour into a test-tube of $\frac{3}{4}$ -inch interior diameter, and about 6 inches long, until filled to within about two inches of the top. Keep the tube warm until the whole of the water, salt, and casein has sunk, and left a perfectly clear fat; now solidify by immersing the tube in water of 15° temperature. When quite cold, notice whether a dimple or hollow cone be formed upon the top; if so, it is a fact of sufficient importance to give rise to suspicion. Pure butter shows only a slight depression, whereas mixtures of a fat having a high fusing point, with butter, cool with a hollow cone; an admixture of 20 per cent.

of mutton or beef fat with butter invariably presents this appearance. If a hollow be formed, the top part of the fat must be refused so as to give a level surface upon which to place the bulb.

Immerse the tube containing the sample in cold water, contained in a beaker of the capacity of 1 litre : the top of the fat must be about $1\frac{1}{2}$ inch below the surface of the water. A convenient method of fixing the tube in position is to pass it through a hole drilled in a piece of wood and placed across the top of the beaker ; by this means two sinking points may be taken at the same time.

Having fixed the tube in an upright position, drop the bulb on to the surface of the fat. The arrangement is now complete, and heat may be applied by means of a Bunsen burner raised so as to just touch the sand-bath. The water should now be stirred at intervals, and the thermometer read off just as the whole of the globular part of the bulb has sunk beneath the fat.

The following results have been obtained by this method ; they are placed without selection in the order in which they were obtained.

Sinking Point with Genuine Butters.

No.				Centigrade.
1	Butter from town-fed cows	35·3°
2	Farm butter from Hertfordshire...	36·1°
3	„ „ „ St. Lawrence...	34·8°
4	„ „ „ Chale	36·3°
5	„ „ „ Newport	35·3°
6	Butter from Ventnor	35·3°
7	„ „ „	35·5°
8	Farm butter from Niton	34·8°
9	Salt butter from Ventnor...	35·9°
10	„ „ „ „	34·8°

No.							Centigrade.
11	Fresh butter from Ventnor	35.1°
12	Farm butter from Chale	35.6°
13	" " " "	36.3°
14	Rancid butter	35.8°
15	Farm butter from Chale	36.3°
16	" " " Ventnor	35.5°
17	" " " "	34.3°
18	Sussex butter	35.5°
19	Normandy butter	35.7°
20	Butter from Ventnor	36.1°
21	" " "	35.3°
22	Jersey butter	35.3°
23	Butter from Guildford	35.7°
24	" " "	35.3°

Average of the 24 samples ... 35.5°
 varying from 34.3° to 36.3°.

Adulterated Butters.

1	Butter from Ventnor, 1s. 2d. per lb.	35.9°
2	" " London " "	42.7°
3	Kiel Butter, 1s. per lb.	38.4°

The sinking point of sample No. 1, as will be seen, is normal; the butter was, however, found on analysis to be highly adulterated with a foreign fat having a low sinking point.

Sinking Point of Fatty Acids from Butter.

1	41.8°
2	42.1°
3	40.5°
4	41.1°

Sinking Points of Fats other than Butter.

1	Tallow from candle	53.3°
2	Butterin (patented)	31.3°
3	Ox fat	from	48.3°
4	„	to	53.0°*
5	Mutton fat	from	50.1
6	„	to	51.6°†
7	Lard	from	42.1°
8	„	to	45.3°
9	Dripping	42.7°
10	„ from beef	43.8°
11	„ „	44.5°
12	„ from veal	47.7°
13	„ mixed...	42.6°
14	Cocoa butter	34.9°
15	Palm Oil	39.2°
16	Stearin	62.8°

Sinking Point of Mixtures.

No. p.c.	p.c.	Found.	Cal.
1 66.7 butter and	33.3 tallow
2 73.0 „ „	27.0 mutton fat
3 10.0 „ „	90.0 „ „
4 85.0 „ „	15.0 ox fat
5 69.8 „ „	30.2 „

Problem : To calculate the sinking point of a mixture of known composition.

Multiply the percentage of the first constituent by its sinking point.

Multiply the percentage of the second constituent by its sinking point.

* Average, 50.6°.

† Average, 50.9°.

Divide the sum of the two products by the sum of the percentage of the two constituents ; or in formula :—

F being fat, and S sinking point,

$$\frac{F_1 \cdot S_1 + F_2 \cdot S_2}{F_1 + F_2}$$

Example 1.—Calculate the sinking point of a mixture of 75 mutton (sinking point, 50·1) and 25 palm-oil (sinking point, 39·2) :—

$$\frac{75 \cdot 50\cdot1 + 25 \cdot 39\cdot2}{75 + 25} = 47\cdot37.$$

If butter be one constituent in the mixture, the formula will be somewhat modified, inasmuch as butter contains, besides fat, on an average, 15 per cent. of water, curd, and salt, which, being removed by fusion, must not be admitted into the calculation.

One part of butter, therefore, is equal to 0·85 part of fat ; the percentage of the butter present in the compound must consequently be multiplied by 0·85, to give per-cents of butter-fat, thus :—

$$\frac{0\cdot85 \cdot B \cdot 35\cdot5 + F \cdot S}{0\cdot85 \cdot B + F}$$

Example 2.—Calculate the sinking point of a mixture of 66·7 of butter and 33·3 tallow (No. 1 of our list of mixtures) :—

$$\frac{0\cdot85 \cdot 66\cdot7 \cdot 35\cdot5 + 33\cdot3 \cdot 53\cdot3}{0\cdot85 \cdot 66\cdot7 + 33\cdot3} = 42\cdot08$$

The sinking point actually found, and that arrived at by calculation, will not often coincide exactly, 85 per cent. being taken as the mean, and not as an absolutely constant proportion of fat in butter.

The method employed by Dr. Hassall * is a modification of the plan described, great precautions being taken to ensure correctness of the result. Instead of a weight, he employs a small glass bulb, having a weight of 0·18 gramme and a volume of about 0·5 c.c. This is placed in the bottom of a test tube, one-third of an inch wide, and four inches high. A little melted fat is poured upon the bulb, and is allowed to cool to keep the float in its position; the tube is then filled with the fat, and a thermometer, graduated in tenths of degrees C., is introduced into the fat in test tube, not into the water surrounding it. The fat is solidified by immersion in water of 13·3° C. for an hour. The test tube is then suspended in a large beaker filled with cold water, and this in its turn heated in a water bath. Thus the temperature rises very slowly and evenly. As soon as the fat is sufficiently soft, the bulbs begin to rise; this Dr. Hassall calls "the rising point." The fat gets clear very soon afterwards, the point of clearance being also noted.

The following results were obtained by Dr. Hassall :—

Points of Fusion and of Clearance of Butter.

	Point of Fusion.	Point of Clearance.
1	34·0	35·7
2	34·2	35·6
3	33·4	35·3
4	32·8	35·1
5	33·6	35·2
6	33·8	36·3
7	34·3	35·4
	Mean 33·7	35·5

It will be noticed that the "point of clearance" exactly coincides with our "sinking point."

* "Food and its Adulterations," p. 441.

filled with the fats to be tested, and after being labelled are put aside to cool. A beaker is selected which fits sufficiently closely into an opening in the water bath, and filling it with water at 65° it is dropped into the opening so as to allow the beaker to be suspended by its rim in the water contained in the bath. The tubes, which are open at both ends, are placed in the beaker, with a delicate thermometer, and a small gas flame placed below the bath, so as to raise the temperature of the water very slowly. As the fat melts in the tubes it rises up in consequence of the water entering at the lower end, and the temperature at which it rises is read off upon the thermometer.

The author's experiments were declared to be very satisfactory, as a repetition with the same fat gave the same temperature in all cases within a degree, and generally within a smaller range.

There are certain precautions mentioned by the author the most important of which are, that the tubes should have notched or oblique ends, so as to allow of the free ingress of the water, and that they should be placed upright in the beaker; the level of the fat should be about a quarter of an inch below the surface of the water.

A plan devised by Mr. Charles Heisch, and published almost simultaneously with Dr. Tripe's, differs mainly in the fact that the melting tubes are drawn out to a capillary point, the capillary portion being about 3 inches long, the rest of the tube having a bore of 0.2 inch.

Mr. Heisch gives the following table, comprising a series in which two portions of each sample were taken in separate tubes:—

*Melting Points.**

			Tube No. 1.		Tube No. 2.	
			Deg. C.	Deg. F.	Deg. C.	Deg. F.
No. 1	36·3	= 97·5	35·6	= 96·
„ 2	31·3	= 88·5	31·1	= 88·
„ 3	31·1	= 88·	31·7	= 89·
„ 4	30·9	= 87·5	30·6	= 87·
„ 5	32·2	= 90·	32·2	= 90·
„ 6	33·0	= 91·5	32·8	= 91·
„ 7	32·2	= 90·0	33·3	= 92·
Lard	38·8	= 102	39·5	= 103
Suet	44·3	= 112	43·8	= 111

Another method described by Dr. Redwood, in a paper read before the Society of Public Analysts, may, under some circumstances, be found of use, as it needs only a drop or two of the fat for each experiment. A small particle of the melted fat is taken upon a glass rod and placed upon the surface of some mercury, and allowed to congeal, the vessel containing the mercury is placed into a water-bath, and a slow heat is applied, the mercury, by virtue of its comparatively good conducting power, acquiring a uniform temperature throughout, which is indicated by the thermometer, and at the same time communicated to the fat. The fat, when the temperature approaches its melting point, becomes partially transparent, and if the stem or elongated bulb of the thermometer be now brought up against it, the moment fusion takes place the liquid fat will run into the channel formed by the repulsion of the mercury and the outside of the thermometer tube. Making use of this method Dr. Redwood made the melting point of two genuine butters to be respectively, “80·5° F. and 81·5° F. as their lowest, and 83·5° F. and 84·5° F. as their highest melting points.”

* *Proceedings of Society of Public Analysts*, vol. i. p. 126.

Mr. Bell takes the melting point in the following simple manner :—" A small portion of the fat, which had a somewhat vitreous appearance, was taken up on the loop of a platinum wire and introduced into a beaker of water placed in a porcelain dish, and the loop brought close to the bulb of a thermometer. The temperature of the water was slowly raised and the temperature read off immediately the fat assumed the liquid condition." (See tables, page 76.) Mr. Bell gives the fusing point at about 32° C.*

Some interesting facts with regard to the well-known curious allotropic conditions through which butter and other fats may be made to pass by the application of heat, in certain definite degrees, was pointed out by Mr. Patrick Duffey, in a letter published in *Chemical News* and reprinted in the *Proceedings of Society of Public Analysts*, page 168, in which it is shown that butter, pork, and mutton fats are capable of assuming at least two distinct allotropic modifications, between which there is a third but less marked condition, which might be a mixture of the other two. Each of these different conditions has a separate fusing point; for the purpose of identification they were designated first, second, and third, according as they were at the first, second, or third of these points.

Mr. Duffey declares that "if a specimen of butter, the second melting point of which lies at 31.2° C., be heated to 60° , and then solidified by a powerful exposure to a temperature not exceeding 14° or 15° , it will melt at 17° . This melting is most readily made visible by plunging a capillary tube containing a portion of the substance into water at that temperature. If the substance be now kept at the range of temperature from 17° to 20° , it solidifies, and in doing so passes more or less completely into an allotropic modifica-

* "Determination of the Melting Points of Butter and other Fats."—*Proceedings of Society of Public Analysts*, p. 51.

tion, the second, which melts only when the temperature rises to 31° or 32° . If the liquid formed by fusion at this point be kept for some hours at a temperature not varying more than two or three degrees on either side of 31° — 32° , it becomes opaque, a great part solidifying as crystals, the third modification, which retain their opacity till the temperature rises to 40° or upwards, according to the length of time at which the substance has been kept at a temperature about 31° — 32° ." The author has "reason to regard the crystals formed in this manner as identical with those deposited in an ethereal solution of butter, which melt at from 53° to 57° , according to their state of purification."

After being heated to upwards of 60° and solidified by cooling below 20° , pork fat melted at 27° — 28° ; passing into the second modification, it melted again at 37° — 38° . Long-continued heating near this temperature converts a small proportion of this substance into the third modification, so that any consequent elevation of the melting point of the mass cannot be determined with precision.

Mutton fat, after an exposure to a temperature presumed to be higher than any of its melting points, and subsequent solidification at a temperature presumedly below all of them, melted at 39° , solidifying again while the temperature rose slowly to 52° — 53° , where it melted a second time, and when kept for some hours within a range of temperature not exceeding 3° on either side of the melting point, solidified again, and then melted only when the temperature rose to 57° . It thus solidified only when the temperature fell below all three melting points, unless the cooling were much retarded. In all cases the temperature at which solidification takes place determines the modification, and consequently the melting point of the substance.

Dr. Dupré and others, as well as we ourselves, have pointed out the effect continued heating has upon the

solidification and subsequent melting point of fats. It may be noticed when a butter has been heated in the air-bath for a long time, in order to drive off water, that the fat will in some instances remain fluid long after it is cooled down to the temperature of the surrounding atmosphere. In consequence of these and other collateral influences, we must advise that a very limited amount of reliance be placed upon the point of fusion in fats, as a proof of their identity or purity.

If a portion of butter-fat which has been cooled down quickly from a long-continued temperature of 100° , be examined under the micro-polariscope, it will be found to consist of a mass of minute and imperfect crystals; if, however, the same fat be cooled down slowly, the usual stellate crystals will be formed, a change from the first to the second may produce in the capillary tubes the so-called first allotropic condition, and bring about an apparent fusion. We are inclined to the belief that these changes in fats are not due to true allotropy. This view is strengthened by the fact that the fusing point, when taken by our method, with a larger quantity of fat, is not effected, as will be seen by the following experiment:—

A test-tube full of butter-fat was kept at 100° for two hours and then cooled down to 15° in running water; the normal sinking point of 35.5 was then found not to have been changed; the gas was then turned out and the whole arrangement left to cool down slowly. The sinking point was again taken, and found not to have changed from the original figures of 35.5 .

CHAPTER V.

THE ANALYSIS OF BUTTER-FAT.

PREVIOUS to the publication of the first edition of this book in 1874, very little was known about the composition of the fat of butter, and very few attempts seem to have been made to arrive at a scientific solution of the question—Is butter chemically different from other fats, and can it chemically be distinguished from them? Upon the physical differences between butter and its fatty relations—namely, colour, smell, melting point, solubility in ether, alcohol, and petroleum spirit, power of turning the plane of polarisation, etc.—many methods had been based to detect admixture of the cheaper fats with the more valuable one; but though some of these methods were not without value, none could be regarded as a safe guide for the analyst, whilst some were positively dangerous, because more calculated to mislead than to point out the truth.

“During the last two years, however, the subject of butter has been much worked at, and its analysis is now as well understood, and as certain, as any other process in the whole range of food analysis.”* We cannot yet, as will be seen in the following pages, with certainty speak as to the constitution of butter-fat, but as far as the detection of

* *Analyst*, August, 1876.

adulterations is concerned, the method to be described has been found all that can be desired.

Urgent as was the necessity to work out a method by which the presence of foreign fats in butter could with certainty be determined ; unwilling as were all public analysts, appointed under the Adulteration of Food and Drugs Act, to risk their reputation in pronouncing an opinion upon samples of suspected butter submitted to them for analysis, because they confessed the absence of a trustworthy method ; and great as must have been the injustice to dealers, who were convicted and heavily fined for selling adulterated butters, though no one could tell in what the difference between genuine and adulterated butter consisted, yet no serious attempt was made to solve the problem. It was by some chemists considered capable of solution, whilst others insisted upon the impossibility of distinguishing between bodies apparently identical in composition.

Thus Mr. Wanklyn, in his treatise on milk, declares that he had no doubt that, if only some one would take the trouble to investigate the subject carefully, he would have a good chance of finding characteristic tests ; and Dr. Muter, as far back as 1870, states in the *Food Journal* that he himself hoped to be able to publish a plan which would lead to the desired end. As late, however, as 1874, before the Adulteration Committee of the House of Commons, the most eminent witnesses emphatically stated that no method was then known. That such was the fact also abundantly appears from all the treatises on food, the authors of which either do not venture upon any statements at all as regards the detection of foreign fats in butter, or, like the late Dr. Smith, they declare that "there are no chemical means."

A saponification test indeed had been employed by Mr. Anderson, founded upon the difference of colour of butter-soap and the soaps of other fats ; but this test, like its

predecessors, belongs to the great class of "doubtful" ones, and like them has never been acknowledged to possess any real value.

In short, an almost total darkness about the composition of butter-fat existed, due, in our opinion, for the most part, to the misleading analysis of Bromeis, quoted in Chapter I., and to be found in all chemical works. This analysis set forth that butter-fat contained 2 per cent. of butyrin and glycerides of other volatile acids; calculated as butyrin only, this number represents 1.74 per cent. of butyric acid, $C_4H_8O_2$ since 302 parts of the butyrin yield 264 parts of the acid. We have also shown that Bromeis's analysis has been found to be incorrect in several most important items. Thus the substance termed by him "margarin" was proved to contain volatile acids, and hence the 1.74 per cent. could evidently not accurately represent the proportion of these acids in butter-fat. Yet, as the presence of volatile acids, such as butyric, caproic, caprylic, and capric acids, was justly considered to distinguish butter from other animal fats, it seemed to be evident that, upon the apparently very trifling quantity of such acids, no test could safely be based by which butter could be with certainty discriminated from other fats. No further steps, therefore, were taken in that direction, as it appeared a hopeless task to look to the volatile acids as foundation of any method; and detection of fatty adulterants by chemical means appeared indeed to be impossible.

Hence it cannot be wondered at that the attention of chemists was more specially directed towards the physical properties of the various fats, and that the methods proposed from time to time were chiefly founded upon these. We will not, however, enumerate and describe them, as they one and all have proved abortive, and are abandoned except by those few who prefer the old system of butter analysis to methods of acknowledged accuracy and trustworthiness.

It would be of considerable interest to know the proportions of stearin, palmitin, and olein contained in butter and other fats, but there are no methods of separating these substances or the acids they yield with anything like quantitative precision. Moreover, if it were really possible to separate them the results would be only of secondary importance, and in no way superior to the indications afforded by the melting point, for mixtures of fats of high melting point and of liquid oils could easily be made containing stearin, palmitin, and olein in the same proportion as these glycerides occur in butter. Tests founded upon such proportions would be quite as fallacious as the specific gravity of milk, if used alone, and not as a corroboration to the results obtained by some more trustworthy method. It should here be remarked that it is by no means certain whether butter-fat really does contain either stearin or the ordinary normal olein. Stearin seems to be entirely absent, and the liquid glyceride present may well be a butyrolein, such as given by Bromeis. Dr. Tidy, in a paper read before the Society of Medical Officers of Health, denied that butter contained more than traces of palmitin, stearin, or olein. But Dr. Tidy does not state what butter, in his opinion, consists of, or upon what grounds his statement is based. Certain it is, that if there is any stearin its quantity must be infinitesimally small, as the fatty acids, either when crystallized from alcohol or precipitated fractionally by acetate of magnesia, do not yield crystals of the composition of stearic acid or a precipitate of stearate of magnesia. But by the former of these methods a beautiful white acid, crystallising in tufts of silky needles, agreeing in physical properties, solubility, etc., with palmitic acid, may be obtained, and this acid seems to constitute a large proportion of the insoluble fatty acids of butter-fat.

The magnesium salt of this acid was found to contain

4.43 per cent. of magnesium, whilst the formula of palmitate of magnesium requires 4.49 per cent., and of the stearate 4.06 per cent.

As many years had passed since Bromeis published the results of the analysis of butter, and as, moreover, as we have seen, several inaccuracies had been pointed out in his figures, we thought it worth while, in 1874, when the necessity for a method was more than usually felt by analysts, to re-investigate that part of the subject which deals with those constituents which are characteristic of butter, namely, the several volatile fatty acids enumerated above, and which, as we have not attempted their separation from each other, we will, for convenience sake, include in the present chapter under the name of *butyric acid*, as this is doubtless the by far predominant representative of the group. We do not, however, wish to convey the impression that butyric acid alone is present.

As the first, and perhaps the most important result of our investigations, we found, that *the amount of butyric acid in butter-fat is very much larger than was formerly believed*, about four times as great as stated by Bromeis.

As the second, pre-eminently practical result, it became clear, that *the amount of butyric acid in butter-fat is very constant*, and nearly independent from the breed of the cow which forms the butter, from the food, the season, the mode of preparation of the butter, and from other conditions, which might have been supposed to exert an influence upon the composition of the fat.

Numerous experiments and determinations have convinced us of the truth of these important facts, and hundreds of analyses, made both by us and the large number of other chemists, who have, since 1874, repeated our experiments, prove their correctness.

It will, we trust, be found interesting to give a sketch of

the path which led us to the above conclusions, though improved methods have now superseded our original one, which was certainly somewhat imperfect.

To obtain the fat in a state of purity, free from the admixtures with which it is associated in commercial butter, in the proportion, on an average of 85 parts of fat and 15 parts of water, curd, and salt, it is merely necessary to fuse the butter in a test tube or small beaker in a water-bath, to allow the water and the solid particles to subside for the most part, and then to pour the fat upon a dry filter, care being taken to keep the aqueous solution in the beaker, as it would pass through the filter and contaminate the fat. The paper and the funnel are first to be heated in the water-bath, or better still, a double funnel, one with a warm water-jacket, is used to keep the fat in a state of fusion. It is also quite practicable to put both the funnel and the small light beaker, in which the bright yellow oil is collected, into the water oven, whilst filtering. If done in the cold air the fat soon solidifies, and filtration, of course, stops. Thus the fat is obtained in a state of perfect purity and quite free from moisture; on drying in the water-bath it does not in the least diminish in weight, and on incineration it leaves no trace of mineral matter. It is allowed to cool, and is then in a state fit for analysis.

All natural fats, as far as is at present known, are mixtures of the tri-glycerides of different acids of the fatty and of the oleic acid series; they are ethers of the alcohol radicle glyceryl, and, like all ethers, they are broken up by the action of caustic potash into an alcohol, namely, glycerin, and the potash salts of the various acids. Thus stearin yields glycerin and stearate of potash, thus,—

$3 \text{ C}_{18}\text{H}_{35} \text{O}_2, \text{C}_3\text{H}_5 + 3 \text{ KHO} = 3 \text{ C}_{18}\text{H}_{35}\text{KO}_2 + 3 \text{ HO}, \text{C}_3\text{H}_5,$
and butyrin splits up into glycerin and butyrate of potash,

$3 \text{ C}_4\text{H}_7\text{O}_2, \text{C}_3\text{H}_5 + 3 \text{ KHO} = 3 \text{ C}_4\text{H}_7\text{KO}_2 + 3 \text{ HO}, \text{C}_3\text{H}_5.$

On the addition of a strong mineral acid, such as sulphuric acid, to the soap obtained by the action of the alkali, the fatty acids are liberated, sulphate of potash being formed. Thus are obtained, partly in solution, partly as precipitate, sulphate of potash, glycerin, fatty acid, and excess of mineral acid. Some of the fat acids, as oleic, palmitic, and stearic acids, are, as we have shown in Chapter I., insoluble in water, whilst others, such as butyric, caproic, etc., are soluble in the same menstruum; the soluble acids possess, moreover, the property of being volatile, and, to distil from their aqueous solution without decomposition; their solubility decreases as the number of carbon atoms they contain increases, and the volatility stands in a similar relation to their composition. Hence in the case of fatty acids, soluble and volatile are synonymous terms.

The simplest plan, which seemed to allow of an accurate, quantitative determination, in butter-fat of the acids, which we comprise under the name of butyric, appeared to be to saponify the fat, to decompose the soap by means of dilute sulphuric acid, and to subject the mixture containing the free acids to distillation. The volatile acids would thus be found in the distillate. This process had been applied many years ago by Chevreul, who thus prepared butyric acid from butter. A quantitative determination seems, however, never to have been made.

The following experiments were undertaken with this view:

Experiment 1.—A weighed quantity of the fat of genuine butter was saponified by means of caustic potash in a boiling flask. The saponification presented many difficulties, since the oil floats on the top, and is but slowly decomposed by the alkaline solution, which, under such circumstances, boils most irregularly and violently, so as either to break the flask or to cause the liquid to run over. After many unsuccessful experiments we at last obtained a perfectly bright and clear yellowish soap, which gelatinised on cooling.

Dilute sulphuric acid was added, and the strongly acid liquid was then subjected to distillation. Here again the bumping of the boiling liquid endangered the success of the experiment. The acidity of the distillate was determined by means of standard soda solution, and calculated as butyric acid. Obtained 6.52 per cent. of butyric acid.

This figure cannot be considered as accurate, since the violence of the ebullition rendered it impossible to carry the distillation to the end, the distillate being still acid when the experiment was stopped. Although incomplete, this first determination proved beyond doubt that the quantity of volatile acids contained in butter-fat was much more considerable than was supposed.

Experiment 2.—9.680 grammes of butter-fat were saponified in a flask as before. The soap was decomposed, the liquid heated until the fatty acids floating on the surface were just fused to a clear oil, which then was allowed to cool and solidify. The fatty acids were then removed and washed by means of boiling water. The filtrate and washings were subjected to distillation, and the acidity of the distillate determined as described. The acidity of the distillate, however, never quite disappears, and when so great a concentration has been reached, that the glycerin in the liquid begins to decompose, the acidity becomes again very considerable, doubtless from the production of acrylic acid. 6.76 c.c. of standard soda solution were neutralised by the distillate. 1000 c.c. of this standard solution are equivalent to 88 grammes of butyric acid; 6.76 c.c. therefore = 0.59488 gramme, or 6.146 per cent.

Experiment 3.—7.494 grammes of the same butter-fat yielded 7.480 per cent. of volatile acids.

Experiment 4.—10 grammes of another butter-fat gave a quantity of volatile acids neutralising 5.79 c.c. of standard soda solution equal to 5.09 per cent. of butyric acid.

Experiment 5.—10 grammes of the same butter as used in 4, yielded 4·796 per cent.

Experiment 6.—6·565 grammes of the same butter yielded 7·452 per cent.

Experiment 7.—7·346 grammes of the same butter gave 7·259 per cent.

Experiments 4 to 7 having been made upon the same sample of butter-fat, prove that constant results cannot be obtained by means of distillation, the percentage of the volatile acids varying from 4·8 to 7·4.

Experiment 8.—Another genuine butter yielded 6·026 per cent. of volatile acids. This distillation was carried on so far, that the glycerin contained in the solution began to char and to be converted into acrolein; but the distillate was still strongly acid, more so indeed than it had been at the commencement of the experiment.

From these determinations, imperfect as they are, it became evident that from 6 to 7 per cent. of volatile acids may be obtained from butter-fat merely by distillation, whilst at the same time it was sufficiently proved that constant results cannot be obtained by following the method described, and that either not the whole amount of the volatile acids can thus be separated, or that the formation of products of decomposition of the glycerin vitiates the result. The great constancy of the melting point strongly indicated a corresponding constancy of the chemical composition. Seeing then, that the direct determination of the butyric acid could not be done with anything like accuracy, we had recourse to an indirect method of estimation.

We have mentioned above, that all natural fats are mixtures of different tri-glycerides, and with the exception of butter, the group of animal fats consists of tri-stearin, tri-palmitin, and tri-olein. With the animal fats we are more immediately concerned, as only these have ever been alleged to be

used as adulterants with, or substitutes of butter, if we except the small quantity of palm oil, used to impart a yellow colour to such mixtures.

The equivalents of these glycerides, and of the acids they furnish on decomposition, being very high and but little differing from each other, theory predicted that they would yield, on saponification and decomposition of the soap with dilute mineral acid, nearly equal amounts of fatty acid. Thus pure palmitin would yield 95·28 per cent. of palmitic acid ; pure stearin, 95·73 per cent. of stearic acid, and lastly, olein 95·70 per cent. of oleic acid.

All fats therefore, being mixtures of these three glycerides, should yield percentages of fatty acids ranging between 95·28 per cent. and 95·73 per cent., or as stearic and oleic acids for the most part predominate, on an average about 95·5 per cent. As the three acids named are insoluble in water, we may therefore assert that *all animal fats except butter-fat furnish 95·5 per cent. of insoluble fatty acids.*

Butter, containing as we have shown, a considerable proportion of volatile acids, which at the same time are more or less soluble in water, should therefore furnish a lower amount of insoluble acids, these being diminished in ratio to the quantity of the insoluble acids.

This reasoning proved to be strictly in accordance with the facts. Numerous determinations of the amount of insoluble fatty acids in animal fats, such as tallow, lard, and dripping, proved the correctness of the theory, results being obtained closely approaching 95·5 per cent., whilst butter yielded on an average of twelve experiments made on different samples but 85·85 per cent., the results ranging from 85·4 to 86·2 per cent. The plan followed was shortly this. A weighed quantity of the fat, conveniently about three grammes, was saponified in a small porcelain basin, by means of a concentrated aqueous solution of potash, the liquid being kept boiling, or

nearly so, over the naked flame and constantly stirred with the glass rod, to intimately mix the oil with the alkaline solution.

The water constantly evaporating was from time to time replaced by distilled water, until a perfectly clear and transparent soap solution was obtained, which was usually the case in about two or three hours. Dilute sulphuric or hydrochloric acid was then added, the fatty acids which separated were allowed to melt, and collected on a weighed filter, washed with a large quantity of boiling water, dried and weighed.

But very shortly after the publication of the results thus obtained we were made aware that our figures, as might have been expected, were for the most part somewhat too low, notably so our average of 85.85 per cent. During an ebullition of two or three hours' duration, in an open evaporating basin a slight loss by spurting cannot be entirely prevented, even when the greatest possible care be taken, the less so, because every bubble of steam, which rises from the aqueous liquid, bursts in the oily layer which floats at the top, and carries not rarely a minute fraction of the fat with it, which in most cases falls back into the basin, but which in others is lost. As we have mentioned, the process of saponification cannot be conveniently carried out in a covered glass flask, as the violence of the boiling in most cases causes loss of the liquid, or even shatters the glass to fragments. This loss by spurting was of course a very serious drawback, and the great trouble and labour and the unceasing attention necessary during saponification rendered the process a by no means easy or elegant one. But all these inconveniences and the source of error were at once removed by a modification introduced by Dr. G. Turner, Medical Officer of Health and Public Analyst for Portsmouth. This modification consisted in the employment of alcohol as a solvent for the alkali necessary

for saponification. As butter most readily dissolves in warm alcohol, the action of the potash is greatly facilitated, both oil and alkali being in solution, and consequently most intimately mixed, whilst the butter-fat merely floated on the aqueous lye, offering but a small surface for action. Saponification in alcoholic solution appears in fact to be nearly instantaneous provided the liquid be warm, but even in cold solutions it proceeds with great speed.

Thus modified, the original, tedious, troublesome, and inaccurate method was at once rendered quick, exact, and even elegant; one which takes neither more time, manipulation, nor skill than the average of analytical methods; it requires indeed scrupulous care, but this can hardly be raised as an objection, seeing that the most exact of methods is rendered valueless without it; it requires, moreover, rigid observation of the rules we will presently refer to, and which are dictated by the practical experience obtained from the analyses of some hundreds of samples of butter we have ourselves made.

Before detailing the method for the determination of the insoluble fatty acids, we will shortly mention the most important results arrived at. The percentage of fatty acids in butter fat, made from the milk of cows of the most varied breed, of different countries, fed with green or with dry food, and in different seasons, varies usually between 86.6 and 87.5, though it in some rare instances falls as low as 86.3, and rises as high as 88.5 per cent. A fair average is represented by the figure 87.3 per cent.

It is thus established that the amount of insoluble fatty acids is a tolerably constant figure, as constant in fact as can reasonably be expected, considering that no animal product can from the nature of animal life be ever invariably the same (excepting of course definite compounds, such as urea, etc.).

Through the labours of Mr. J. A. Wanklyn, as is well known, the analysis of milk, as regards the detection of added water, has been placed on a sound basis, inasmuch as he pointed out that the percentage of "solids not fat" was nearly constant. No milk, yielded by an undoubtedly healthy cow, has ever been found to yield less than 9.0 per cent. of "solids not fat," although samples containing as much as 11.3 per cent. are to be met with. A milk containing less than 9 per cent. may safely be declared to be adulterated with water.

Similarly we are now in a position to say, with even a greater degree of probability, that no sample of butter-fat can be declared to be pure and genuine, unless the percentage of insoluble fatty acids be lower than 88.5 per cent. But just as from 20 to 25 per cent. of water may be added to milk of the very best quality, in order to depress it to the lowest level, namely 9 per cent. of solids not fat, so about 15 per cent. of foreign animal fat may be added to a butter rich in soluble acids, the product being equal to the lowest quality butter. In all similar cases, the dealer gets the benefit of the doubt, but there is a certain limit which he cannot overstep with impunity.

A judicious addition of any soluble substance, such as cane or milk sugar to diluted milk, raises the percentage of the "solids not fat" to their proper level, and adulteration would in such cases be entirely overlooked, or could only be detected by a careful analysis of the dissolved constituents. In the case of butter, however, it is not possible to evade analysis in a corresponding manner; it might approximately be done by the addition of a tri-glyceride of a soluble acid, but such glycerides are only to be obtained from butter, or synthetically. But even then, as will appear from some observations on the chemical constitution of butter-fat, it would not be difficult to extract such added glyceride from the butter.

Practically therefore it is impossible, by even scientifically conducted methods of adulteration, to evade detection by analysis.

We think it proper, however, here to mention the fact, that there is *one* fat which might perhaps be used to adulterate butter, which contains, according to our analysis, an equally low percentage of insoluble fatty acids, namely, cocoanut oil. All other fats examined, animal or vegetable, as the fat of mutton, beef, or pork, palm oil, cocoa butter, olive and other oils, yield the normal percentage of 95.5 per cent., or figures closely approaching it.

DESCRIPTION OF THE METHOD.

The small beaker containing the pure butter-fat obtained by filtration as described, is weighed, and a quantity approaching three or four grammes is taken out by means of a dry glass rod, and transferred into an evaporating dish. The rod is put into the dish, the beaker again weighed, and the quantity of butter-fat taken thus ascertained by difference. The dish should be a deep one, about five or six inches in diameter, and well glazed, one with glazed edges being preferable. The fat is then fused on the water bath, and about 50 c.c. of alcohol of about 85 per cent. are added. Methylated spirit may be used, provided it be free from resinous matter, which it so frequently contains. As soon as the alcohol gets warm, the butter-fat easily dissolves, especially when gently stirred with the glass rod, forming a clear yellow solution. Whether the whole of the fat be dissolved or not, a small bit of pure caustic potash or soda, weighing about one or two grammes, is now added and agitated in the liquid, in which it but slowly dissolves, care being taken not to allow the alcohol to be heated to its boiling point, as loss by spurting would be inevitable. Saponification proceeds rapidly, and is,

in the case of butter-fat, evinced by the strong agreeable smell of butyric ether evolved, resembling the odour of pine-apples.

After a minute or two, a few drops of distilled water are added to the alcoholic liquid. If, thereby, a turbidity makes its appearance, caused by undecomposed fat, the liquid is heated a little longer, the turbidity dissolving in the excess of alcohol. Small quantities of distilled water are added from time to time, until a considerable addition of it to the solution of soap no longer causes any precipitate of fat. It must be remembered that water takes part in the reaction which ensues, and if the alcohol be too strong, even the most prolonged heating would not effect perfect saponification.

Another mode of procedure is to make a saturated solution of caustic potash or soda in alcohol, and use about 5 c.c. of this solution. This has some advantage over the addition of the solid alkali, as spurting is not so likely to happen, and the introduction of impurities hidden in the stick potash or soda is impossible; besides which carbonates, if present, are precipitated in the alcohol, and any danger of effervescence which may be caused by the escape of carbonic acid when the acid is added, and which may render the decomposition too violent, is also avoided. When the alkali is added in alcoholic solution, the whole may be allowed to evaporate to dryness, providing that the water-bath be not too hot, without danger of loss by spurting, and usually a clear soap solution is obtained when water is added.

Saponification is complete when any amount of dilution does not alter the transparency of the liquid. Should it happen that the water has been added too quickly (which can only occur if the necessary care has not been bestowed upon the process), fat separates in the form of oily droplets, which now no longer dissolve in the too dilute alcohol. In

this case an additional quantity of alcohol may effect the solution, frequently only after the liquid has been concentrated by evaporation, but it is preferable to begin the experiment afresh with a new quantity of butter-fat.

The soap is then heated on the water-bath until all smell of alcohol has disappeared; the dish is nearly filled with water, in which the gelatinous soap, which has separated on concentrating the liquid, readily dissolves. Dilute hydrochloric acid is now added to strong acid reaction of the liquid, to liberate the fatty acids. These rise quickly to the surface as a white or yellowish creamy precipitate, whilst a strong disagreeable smell of butyric acid or its relations is given off. It will be observed, that unless the alcohol be removed completely, or very nearly so, the risk of losing some of the fatty acids is caused by their being kept dissolved in the alcohol.

The separated fatty acids are heated on the water-bath for about half-an-hour, until they are perfectly fused into a clear oil, and until the acid liquid below is nearly clear. During the process of fusion it is well to avoid allowing the water to evaporate much, as by so doing the acids come into immediate contact with the dry dish, and can be removed only with considerable difficulty. The water in the water-bath should not be boiling.

Meanwhile a filter of about five inches in diameter, of the best and closest Swedish filter paper, has been dried in the water-box, as well as a filter weighing-tube with ground stopper, and a small beaker. The beaker, the filter-tube, and the tube and filter, are now weighed, the weight of the beaker plus filter being thus obtained. The paper, on account of its being eminently hygroscopic, cannot of course be weighed directly, but must be enclosed in the tube, or between two watch-glasses. It is equally inadmissible to counterpoise it by another filter of the same size and paper, as is frequently

recommended for similar operations, partly because of its affinity for water, partly because two filters, cut with the same stamp out of the same paper, never are of equal weight, but often many centigrammes different.

The filter paper must be of the very best quality, and of close texture, so as to allow even boiling water to filter only drop by drop through it. Only with such paper—which must, moreover, be carefully adjusted to the funnel—is it possible to obtain a perfectly clear filtrate, free from even the minutest traces of fatty matter. Through such filter paper the filtration is somewhat slow; but this can only be considered an advantage, as several samples may be examined at the same time, whilst loose paper would both allow a small proportion of the fatty acids to pass through it, and filter with such rapidity that it can hardly be kept full from the wash-bottle. A double filter may often be used with advantage.

The filter being moistened and partly filled with boiling water, the fatty acids and the acid liquid below these are now poured upon it. As soon as all liquid has been removed into the funnel, the basin is washed with boiling distilled water, until every trace of oil has been transferred upon the filter, the glass rod being freed from oil in a like manner. It might be supposed that the fatty acids would obstinately cling to the vessel, and that a loss would thus be incurred. This, however, is by no means the case, for boiling water takes away every trace of the fat, especially when the stream of boiling water from the wash-bottle is directly turned with some force upon the particles to be dislodged. Should, however, any doubt arise as to whether all fat has been removed from the basin and the glass rod, these may be dried on the water-bath and washed with ether, the ethereal solution being afterwards either evaporated in a weighed beaker, or added directly to the fatty acids when taken out of the funnel. The quantity thus obtained is, however, very

trifling, and amounted in two experiments we made to only 0.0008 and 0.0016 gramme.

The fatty acids which are now upon the filter are well and thoroughly washed with boiling water. It is quite easy to whirl them round on the filter, and to incorporate them most intimately with the water. The filter must never be more than at most three-quarters filled. It is a good plan when making the first fold in the paper to bring the edges not quite even, and to double with the lower fold inside, so that the capillary tube which is formed by the inside crease shall not quite reach the top of the filter when placed in the funnel. By this means, if any of the oily fat rises, as it sometimes does by capillary attraction, it will not pass over. From 700 to 1,000 c.c. of boiling water are mostly required to remove all soluble acid from the oil, it being indispensably necessary to wash until delicate litmus tincture is no longer reddened by a few cubic centimetres of the filtrate, which ought never to be less than the smaller quantity named, if three grammes of butter-fat be taken.

All water is allowed to run out of the funnel, which thus retains only the fatty acids in a melted condition. The funnel is then plunged into a beaker filled with cold water, so that the levels of the fat inside and the water outside the funnel are the same, and when the fatty acids are quite solidified the filter is carefully taken out of the funnel, loosely stood upright in the small weighed beaker, and dried in the water oven. After two hours' drying the weight is taken for the first, and after two and a half hours for the second time, when it mostly will be found to have remained constant. If not, the fat must be dried for a further period, until the two last weighings agree to within one or two milligrammes. The quantity on the percentage of the insoluble fatty acids is thus arrived at.

Should it, from any cause, be found necessary to interrupt

the analysis, whilst the fat is still on the filter and not perfectly washed, the funnel should be plunged into water as described, keeping the filter-paper moist. No loss of fatty acids need then be apprehended.

In case the washing of the fatty acids be not continued sufficiently far, the drying to constant weight proceeds afterwards considerably slower than it does in a properly executed experiment; it may stretch over a period of many hours, during which some change of the fatty acids by oxidation may be incurred. This is doubtless due to the presence of caproic and similar acids in butter, which, being only very sparingly soluble in even boiling water, are obstinately retained by the insoluble fatty acids, and if not removed by washing, they are slowly volatilised at the boiling point of water.

If a few drops of water should happen to have remained in the filter when removed to the weighed beaker, they will sometimes collect on heating below the melted fat, and volatilise but exceedingly slow. In such cases it is best to follow the advice of Dr. Muter, and to add a drop or two of alcohol, when the removal of the water proceeds without difficulty.

The following may be taken as an instance of the determination of the insoluble fatty acids in genuine butter-fat:—

Beaker and butter-fat	39.3226
Beaker	36.0395
Butter-fat taken	3.2831
Tube and filter	15.4281
Tube empty	14.8451
Filter	0.5830
Beaker empty	20.9967
Beaker and filter	21.5797

Beaker, filter, and fatty acids (2 hours)	...	24.4642
" " " (2½ ")	...	24.4500
" " " (3 ")	...	24.4505
Fatty acids...	2.8703
Fatty acids, 87.42 per cent.		

It is to be borne in mind that the fat acids are comparatively unstable compounds, not as unalterable by keeping or exposure to the air as are the majority of the substances obtained in mineral analysis. It cannot, therefore, be wondered at, that the weight of these acids does not keep absolutely constant on heating to the boiling point of water, but that it varies to some extent, according to the time they are exposed in a fused state to the action of oxygen. This change, however, takes place very gradually, and does not by any means prevent accurate determination, as will be seen from the following figures :—

Beaker and fatty acids after	2 hours' drying	...	24.4642
" "	2½ "	...	24.4500
" "	3 "	...	24.4505
" "	3½ "	...	24.4504
" "	4½ "	...	24.4504
" "	6 "	...	24.4517
" "	7 "	...	24.4556
" "	11 "	...	24.4553
" "	17 "	...	24.4526

After 7 hours' drying at 100° C., the fatty acids kept decreasing slowly, and after 22 hours they again weighed as much as after 2½ hours. After two days the decrease became much more marked, the fatty acids turning deep brown, and emitting a highly rancid odour. It will be noticed that there is no difficulty in obtaining the correct weight, as the changes are but very gradual and slow. The increase which first

takes place is no doubt due to the absorption of oxygen, compounds being formed which, on continued heating, slowly volatilise.

The following list contains some of the results obtained by means of the method described. We might add more figures, but refrain from 'doing so, to avoid unnecessary repetition :—

Insoluble Acids in Genuine Butter.

Per cent.	Per cent.	Per cent.	Per cent.
87.9	86.8	86.8	87.5
87.1	86.8	87.3	87.8
87.2	87.2	87.0	86.9
87.5	87.3	87.5	87.8
87.8	87.3	87.6	87.5
87.0	87.2	86.8	88.2
87.1	86.9	87.1	86.1
87.1	87.2	87.2	87.3
87.3	87.3	86.9	
Average	87.24 per cent.

Whilst giving the above figures as representing the percentage of fatty acids in genuine butter-fat, we by no means wish to convey that higher figures might not be yielded by some samples.

Thus the analysis of eight samples of Normandy butter, all obtained from the same source, yielded the following figures :—

Per cent.	Per cent.	Per cent.	Per cent.
89.1	89.4	88.6	88.9
89.6	88.7	88.6	88.7

But as these butters were all of the lowest quality, partly highly-coloured either by means of palm-oil or some other vegetable colour, and as they, moreover, were all obtained

from the same merchant, we think we are fully justified in doubting their genuineness. Several similar cases have come under our notice, but in every instance the butters were imported from abroad, and no guarantee for their purity existed. On the other hand, we have frequently determined the quantity of insoluble fatty acids in articles acknowledged to be mixtures, such as "butterine," and always found the figures to come to about 92 or 93 per cent., or even more, corresponding to an addition of foreign fat amounting to two-thirds to three-fourths of the whole article.

Butter-fat, when exposed to the action of the air, is considerably changed in appearance, slowly at ordinary and quicker at higher temperatures. It becomes perfectly white and tallowy, acquiring a very acrid, rancid smell. One might be inclined to think that a change so greatly altering and apparently destroying all characteristics of butter, could not be without a deep influence upon its composition and upon the percentage of the insoluble fat acids. Now, although this change doubtless influences and alters the quantity of the fatty acids, yet it takes place to so slight an extent as not to interfere in the least with the accuracy of the method, as will be apparent from the following determinations.

A first-class butter, which yielded in its fresh state 87·48 and 87·57, or on an average 87·52 per cent. of insoluble fatty acids, was exposed to the air for about four months, a thin layer being spread out on a glass plate properly sheltered from dust and moisture. The white, tallowy mass into which the butter was found to be converted at the end of that time, was again analysed, and yielded 87·90 per cent. of fatty acids. Of course butter could not be sold in so decomposed a condition as was presented by the sample analysed. The above results, which are corroborated by many similar instances, therefore show decisively that the percentage of insoluble fatty acids is not altered to any great

extent by the decomposition of the butter. Mr. Bell made analogous experiments, and came to precisely similar results.

To ascertain the influence of the food of the cow upon the amount of fat acids in butter, Dr. Turner caused a cow to be fed for a considerable length of time, as far as practicable, with oil cake, with the view, if possible, to raise the percentage. The butter was analysed by Dr. Turner, Dr. Muter, and by each of the authors. The following are the results :—

86·22 per cent. (T ^a)	86·41 per cent. (H ^a)
86·23 „ „ (H ^a)	87·1 „ „ (A ^a)
87·2 per cent. (M ^b)	

After a week the butter was again analysed, and furnished the following results :—

86·6 per cent. (H ^a)	86·8 per cent. (H ^a)
87·0 per cent. (T ^b)	

Thus the determinations conclusively prove that the percentage of the insoluble fatty acids does not rise even under that kind of food, which might be supposed to exert a deep influence upon the composition of the butter. We shall again have occasion to refer to the above figures. (See page 61.)

As among the figures contained in the table given above there are represented winter and summer butters, and specimens of the best quality of fresh and the worst of salt butter ; of the finest Aylesbury and the most inferior Dutch or Brittany ; English, Irish, French, and German, it may safely be asserted that genuine butter, of whatever description or name, always yields approximately the same percentage of fatty acids. Exceptions may perhaps now and then be found, but if they do occur they are very rare, and may doubtless, as in the case of milk, be explained by illness

of the cow or by gross errors in the mode of feeding. Butter, moreover, is never practically made from the milk of one single cow, but of the united cream yielded by a whole herd, and as in the case of milk analysis the excuse on the part of the dealer cannot be considered sufficient, that an abnormal cow is the producer of a suspected butter.

The process for determining the percentage of the insoluble fatty acids may of course be modified. Thus the idea may occur to perform the washing of the fatty acids in a flask, instead of upon a filter, and some may even be disposed at first sight to give the preference to flask washing. So much care and attention is required for our process, that a great deal of trouble may seem avoidable, if instead of washing the acids upon a filter for half an hour or an hour, by means of boiling water, this washing is done simply by shaking the melted mass with boiling water in a flask, allowing the oil to rise to the top and to solidify, when it may seem easy to pour off the liquid from the cake of acids.

This modification is indeed strongly recommended by Dr. Muter, and we are obliged to discuss this trivial question at some length, because he insisted that only by the flask-washing accurate results could be obtained. Dr. Muter based this opinion especially on the fact that his results were considerably higher than those published by us in the first edition of this little work, and which, as we have mentioned on page 46, showed on an average but 85.85 per cent. of fatty acids, while Dr. Muter declared 88 to be a fair proportion. He inferred that we had incurred a considerable loss (which indeed we had). But he believed he had found the sources of this loss, first in the firm adhesion of the fatty acids to the basin, wherein the saponification takes place, from which they could not, in his opinion, be properly removed by washing; and second, in the circumstance that a filter could not perfectly separate the oily liquid from the

acid aqueous solution, some of the fat being alleged to be lost by creeping through the pores of the filter. But both these conclusions are, as we have shown, fallacious. Ether does not extract more than at most two milligrammes of fat from the glass rod and basin, provided they are properly washed; the filtrate is clear and bright, and remains so on standing, no oily drops being visible even when examined under the high powers of the microscope, provided the filter-paper is well selected, close and firm, and of the best possible quality. Dr. Muter, moreover, compares his results with figures which we have long acknowledged to be defective, because directly after the introduction of alcohol as a solvent for the fats, it became evident that the loss by spurting during the long-continued boiling amounted to 1 or even 2 per cent. It was only this spurting, which was unavoidable, which caused the low results we at first obtained and published, and which we subsequently, whenever the occasion arose, acknowledged. As soon as this source of error was avoidable and done away with we got results by the filter wash method, which are practically identical with those yielded by the flask-washing. As an instance we may here again refer to the analysis of the sample of oil-cake butter, quoted at page 59; the figures marked (*a*) were obtained by filter washing, those marked (*b*) by flask washing, by Dr. Muter himself. They approach so closely to our own results as to be within the limits of experimental error.

While, therefore, we readily concede to the flask washing if properly done an accuracy equal to filter washing, we yet must point out some sources of danger which must carefully be guarded against when the former process is employed, and into which Dr. Muter himself has fallen. First, the solidified fatty acids cannot simply be separated from the aqueous solution by straining off the latter; the liquid must necessarily be passed through a filter, which must

either be a dried and weighed one, or which afterwards must be freed by means of ether from the small quantity of fat adhering to it. To strain *off through a bit of muslin* without filtration, as recommended, is quite inadmissible, as in all cases a milky liquid is obtained, which contains in suspension a notable quantity of fatty acids; as Dr. Muter employs, however, a comparatively large quantity of fat (ten grammes), this loss is somewhat diminished in importance, but still it is avoidable, and *ought* not to be admitted. Secondly, as it is necessary every time to cool down the water, in order to solidify the fatty acids, it is evident that the washing is really done with *cold* water, and it is by no means impossible that part of those acids which are but slightly and with difficulty dissolved by even hot water, separate again on cooling. In fact it may easily be observed that the liquid is more strongly acid before it is quite cool than after the solidification of the fatty acids. Hence a very much larger quantity of water ought to be used for washing, than when boiling water is used, and filtered off as such. As for about three grammes of butter 700 c.c., or even more, of boiling water are required to remove all soluble acid, ten grammes of butter-fat ought to be washed with at least $2\frac{1}{3}$ litres of boiling, and a much larger quantity of cold, water. But Dr. Muter takes no more, and even less than one litre of cold water! Hence it is obvious, that his results are too low from loss, and too high from incomplete washing. These errors may counterbalance each other, but not necessarily so, and in general there will be a tendency to get results higher than by the other method, because a large proportion of really soluble acids has not been removed, and does not volatilise on heating to 100° C., from so considerable a quantity of fatty acids as is yielded by ten grammes of fat.

But we know from experience that the results obtainable by either process do as nearly as possible correspond, if equal

care be taken. As filtration cannot under any circumstances be avoided, we think it is easier and quicker to wash on the filter. Trivial as these points are, and without bearing on the general question, they have been lately so much enlarged upon that some mention in this place seems necessary.

From the percentage of the insoluble fatty acids, whether obtained by filter or flask washing, it is easy to draw conclusions as to the genuineness or otherwise of any given sample of butter. If the quantity of fatty acid be lower than 88 per cent., the butter must be declared to be genuine, although, as we have explained on page 49, some foreign fat *may* be present in small amount, since good butter, with a low percentage of fatty acids, bears the addition of about 15 per cent. of foreign fat to raise it to the highest limit. If, however, the fatty acids are higher than 88·5 per cent., we conclude that adulteration has taken place, and from the difference between the amount of fatty acids in butter-fat, and in other fats, the addition is calculated. But whilst a butter of 88·5 per cent. is passed as genuine, we base the calculation, in case sophistication is proved beyond doubt, upon a lower figure, namely, 87·5 (following in this respect the plan recommended by Dr. Muter), assuming that the original butter was of average composition, and not exceptionally rich in fixed fatty acids. The analyst may find it convenient in such cases both to state the minimum percentage of adulteration and the amount of foreign fat, which must have been added to butter of average composition. This is done in the case of milk, and the calculation in the case of butter is entirely similar. An adulteration of 100 per cent., *i.e.*, the substitution of any foreign fat for butter would raise the normal amount of fatty acids by 8 per cent. Let a be the percentage of fatty acids found, then the amount of adulteration $A = \frac{100(a-87\cdot5)}{8}$ or $X = 12\cdot5(a-87\cdot5)$.

Thus we arrive at the percentage of foreign fat contained in the fat of butter. But as the analyst is required to state the amount of adulteration in the butter as sold by the dealer, a further calculation has to be made, since butter contains on an average 15 per cent. of water, curd, and salt, and 85 per cent. of real butter-fat. Now, since by preparing the fat in its pure state we separate these impurities from it, the percentage of foreign fat is greater in the pure glycerides, as used for analysis, than in the butter vended by the dealer.

The above formula gives the percentage of foreign fat in the fat analysed. By subtracting this from 100 the proportion of pure butter-fat contained in the mixture is arrived at. If this be called B, then the quantity of real butter corresponding, C, is $\frac{100 B}{85}$ or $C = 1.1765 B$.

Then the actual percentage of adulteration in the commercial butter is $= \frac{100 C}{A + C}$.

Practically, butter never seems to be adulterated with small proportions of foreign fats, but usually the percentage of adulteration is exceedingly large, from 60 to 80 per cent. This may to a large extent be explained by the fact, that it is very difficult to mix, on a small scale, butter with any fat, so that the resulting product still retains its buttery appearance. The dealer, therefore, never, as far as we are aware, adulterates the butter he vends, but it is a special business, a separate branch of manufacture to prepare such mixtures, upon which names like "Butterine," "Oleo-margarine," "Save Butter," etc., have been bestowed, and which are extensively manufactured on the Continent. No objection can of course be raised against such mixtures if they are but sold and acknowledged as such, but frequently, as soon as the article is retailed, it assumes the name of "Butter," to which it has no right.

Hitherto we have only treated of the practical side of the subject, that part, namely, which relates to the detection and the quantitative determination of adulteration with foreign fat. We have shown that the percentage of fatty acids is lower in butter than in any other animal fat, and upon this difference the whole method is based. To whatever cause this difference may be due, and whatever may be the names and properties of those substances which cause it, the practical bearings of the method are not influenced by them. But from a scientific point of view it is certainly a matter of great interest to ascertain the cause of this depression.

From the somewhat crude distillation experiments quoted on page 43 we concluded, in accordance with a preconceived opinion, that this deficiency of insoluble acids was due to the presence of soluble acids; in fact, as will be remembered, we were led to the determination of the insoluble acids, because by distillation we were able to separate considerable percentages of volatile acids. It must be admitted, however, that the acidity of the distillate might well have in part been due to the formation of acrylic acid, by the action of sulphuric acid upon the glycerin. It was suggested, seeing this weak point, by Mr. J. A. Wanklyn, that butter might differ from other fats merely by its being a di-glyceride, or a mixture of tri- and di-, or even mono-glycerides; and this suggestion bore no marks of improbability.

To settle this point, it seemed desirable to get trustworthy determinations of the amount of soluble acids yielded by butter-fat. The direct separation by means of distillation having given doubtful and inaccurate results, various indirect plans of determining the quantity of these soluble acids were adopted by Dr. A. Dupré, F.R.S., Dr. Muter, and ourselves.

Dr. Dupré's highly interesting experiments (*Analyst*, 1876, page 87) were conducted according to two separate plans. Butter-fat, when heated with water for four or five hours in a sealed tube to 260° or 290° C., splits up into glycerine, soluble acids, and insoluble acids. A strong silver tube, with screw ends, was employed, about 5 grammes of fat being decomposed in each experiment. "After cooling the tube was opened, and the contents washed into a beaker, or latterly a flask, as recommended by Dr. Muter, and the insoluble fatty acids thoroughly washed, dried, and weighed, without removing them from the flask or beaker. The silver tube was washed out with ether, and the amount of fatty acids thus obtained added to that found as above. The aqueous filtrate containing the soluble fatty acids and the glycerine was neutralised with barium carbonate, boiled, filtered, and evaporated, at first on a water-bath, finally *in vacuo* over oil of vitrol. The residue obtained was then weighed, and the glycerine present extracted with alcohol, or expelled by prolonged heating to a temperature of 130° C., and the rest again weighed, the loss being taken as glycerine. Finally, the residual barium salt was converted into sulphate, from which the amount of soluble acids present could be calculated. Neither of these processes is, however, quite satisfactory; in the first some barium salt is dissolved by the alcohol; in the second the glycerine cannot be all expelled without danger of decomposing some of the barium salt.

"The general results of these experiments, I have already stated, viz., that they show the presence of a notable proportion of soluble fatty acids." Dr. Dupré, in four experiments made on different butters thus obtained 5.3, 6.4, 5.33, and 5.8 per cent., mean of the four, 5.70 per cent., and glycerine on an average 11.69 per cent.

The second process adopted by Dr. Dupré, which he

believes "leaves nothing to be desired on the score either of facility of execution or of accuracy," is shortly described, as follows:—A weighed quantity of butter-fat is saponified in a strong closed flask by means of a measured volume of standard alcoholic potash, 25 c.c. of a solution of the ordinary standard strength being used to decompose 5 grammes of the fat. The caoutchouc stopper with which the flask is closed must be firmly tied with string. After heating in the water-bath for about an hour the contents of the small flask are carefully washed into an ordinary flask, the alcohol is dissipated by heating, and 25 c.c. of a standard sulphuric acid, of somewhat greater strength than the alcoholic potash, are added. The fatty acids which are thus liberated are allowed to solidify, and the acid liquid containing the soluble fatty acids and the excess of free mineral acid is passed through a filter. The insoluble fatty acids are washed in the flask, and weighed in the flask after due drying, the small quantity on the filter being extracted by means of ether, at a temperature of 105° C. Thus the quantity and the percentage of insoluble acids are arrived at. By simply determining the acidity of the filtrate and subtracting from the total acidity the quantity corresponding to the excess of acid employed, the proportion of soluble fatty acids is arrived at, which are calculated as butyric acid.

Thus Dr. Duprê found that "butter-fat really does contain from 5 to 6 per cent. of soluble fatty acids."

He also found that, if the saponification took place in an open flask a considerable loss of butyric acid took place, some butyric ether being volatilised, as may readily be perceived by the smell. This loss amounted to as much as 0.76 per cent. We were led to a similar result by direct determination, by Berthelot's method, of the butyric ether distilled off during saponification.

In no case do Dr. Dupre's results add up to 100.

Dr. Muter came to the same conclusion as did Dr. Dupré, the method employed by him being a far more indirect one, and certainly less accurate. A comparatively large quantity of butter-fat, ten grammes, was saponified in an *open* flask by means of alcoholic potash, and the soap decomposed by the addition of sulphuric acid, the alcohol having been previously driven off. The insoluble fatty acids were washed in the flask, dried, and weighed. The liquid containing the soluble fatty acids was made up to 1,000 c.c. In one portion the total acidity was determined, due to free sulphuric and soluble fatty acids. In a second portion the total amount of sulphuric acid, both free and combined, was precipitated by means of chloride of barium, the precipitated sulphate being collected and weighed as usual. Lastly, a third quantity was evaporated, the free sulphuric acid driven off by strongly heating the residue, the mineral matter being taken as sulphate of potash. From these last two data the amount of acidity due to free sulphuric acid was ascertained, which, subtracted from the total acidity, yielded the proportion of acidity due to soluble butter acids.

It will be observed that this process is in several points open to objection, inasmuch as a portion of the volatile acids is necessarily lost in the form of butyric ether during saponification in the open flask, and as the residue calculated as sulphate of potash is never of sufficient purity to allow of its being taken as such. But these objections might easily be avoided by saponifying in a closed flask and determining by precipitation the proportion of sulphuric acid in the residue obtained by evaporation. There are, however, graver objections inseparable from the process, namely three different determinations, gravimetrically and volumetrically, involving a great many different manipulations, have to be made, and small figures, obtained by subtracting comparatively large amounts from each other, be calculated as volatile acids.

Yet Dr. Muter's results unquestionably prove the correctness of the conclusion at which we originally arrived by slender evidence, namely, that butter contains a very notable quantity of soluble acids.

Lastly, we have, by adopting a different method, come to the same result. The liquid which is obtained after the insoluble fatty acids have been carefully washed, as in Dr. Dupré's or Muter's process, is rendered alkaline and concentrated by evaporation. It is then made up to a known bulk, which may be small, say 250 c.c. In one portion of this liquid the amount of alkalinity is determined by means of decinormal sulphuric acid. The rest of the liquid is evaporated and incinerated. Thus the butyrate is converted into carbonate of potash, the sulphate being not, of course, altered. The alkalinity after incineration, diminished by the alkalinity before incineration, indicates the proportion of organic acids present. It must be remarked that the liquid, before being evaporated, must be rendered distinctly alkaline, as from a neutral liquid notable quantities of butyric acid are volatilised. This method is simple and satisfactorily accurate.

Not so, however, we found a method which has lately been recommended for the determination of mineral acids in vinegar, and which is based upon the action of mineral acids on methylaniline violet. This colouring matter was said to be turned green by mineral acids, but to remain unchanged by organic acids. Thus it would merely have been necessary to determine the total acidity, litmus being used as an indicator, and second, to use methylaniline violet, the difference in the two determinations being calculated as organic, in the case of butter, butyric acid. The colouring matter alluded to does indeed turn green by the addition of mineral acids, but it is so little sensitive, that comparatively large quantities of acid are required to produce any visible change.

Its use may be indicated, when one or two per cent. of acid need not be considered, but it is quite inadmissible for accurate determinations.

There is no longer any doubt, therefore, that a notable proportion of soluble acids is present in the fat of butter. Yet practically the results, obtained in the multiplicity of ways described, appear to us to possess but little value, and we cannot concede to the determination of the soluble acids so great an importance as was attributed to them by Dr. Muter, who suggested that they should always be determined besides the quantity of insoluble acids, in order to have a check or corroboration upon the estimation of the insoluble acids. The following are some of the reasons which induce us to place little value upon the soluble acids. We do not, however, wish it to be understood that we altogether deny the usefulness of their determination, which in some few cases, where as much evidence is desirable as it is possible to bring forth, may really be indicated.

A numerical determination cannot be used to corroborate another one, and if necessary to correct the results obtained in another way, unless it is at least as accurate as that which it is meant to corroborate. But since exact and decisive quantitative results have not been hitherto obtained by the employment of either of the methods just sketched out, for the estimation of the soluble acids, and as moreover any figures, inaccurate as they are, can only be arrived at by the expenditure of much trouble and time, and as, on the other hand, the determination of the insoluble acids presents no difficulty whatever, whether the filter or the flask washing be employed, we cannot but come to the conclusion, that the determination of the soluble fatty acids either as corroboration of the insoluble acids, or used alone, is far inferior in accuracy to that of the insoluble fatty acids. Practically their determination is useless, and when analyses are to be executed with dispatch, in large

numbers, such as not infrequently pour in upon the Public Analyst, every unnecessary step, be it ever so small, must be avoided. Conceding even, for sake of argument, an equal accuracy to the determination of the soluble acids, as to that of the insoluble acids, yet the latter is to be preferred, because the quantities obtained are larger, because something tangible is obtained, and the characters of the fatty acids, such as smell, colour, and melting point may be noted if necessary, whilst the determination of the soluble acids being an indirect one no tangible substance is extracted from the butter, and because, lastly, the results are obtained easier and quicker.

A stronger reason against the introduction of the determination of the soluble fatty acids, in order to detect adulteration, is the following : The soluble acids can only be washed out of the insoluble acids with great difficulty. Boiling water is absolutely indispensable if this washing is to be done thoroughly, and loss of the soluble acids by evaporation is therefore hardly avoidable. The saponification is to be performed in a closed flask, because butyric ether largely escapes if the vessel be open ; the washing has to be done under the same precautions, and yet the filtering or the pouring off must bring along with it loss and error, however small.

If, however, the washing is not properly done (and it is most difficult to wash even 10 grammes of butter acids thoroughly and efficiently, as no less than $2\frac{1}{2}$ or 3 litres of boiling water are requisite), part of the soluble acids remains with the insoluble members of the group, and slowly volatilises on drying at 100° C. ; thus no error, at least no serious one, is introduced into the determination of the insoluble acids, but that of the soluble becomes utterly wrong, and unworthy of any importance being attached to it. In the large bulk of wash water necessarily used accurate determination of the minute quantities of soluble volatile acids is in itself an impossibility.

Thus we conclude that the determination of soluble acids is *no* sufficient corroboration to that of the insoluble acids, and that the amount of the latter alone need be known, in order to enable the analyst to form an opinion about any given sample of butter.

The following table shows the quantities of soluble acids corresponding to different percentages of insoluble acids, assuming that butter-fat consists merely of tri-butyrin and tri-stearin or olein. Of course the figures are only approximate, as so large a proportion of the insoluble acids consists apparently of palmitic acid.

<i>Insoluble Acids.</i>	<i>Soluble Acids corresponding.</i>
86 per cent.	8.88 per cent.
87 ,,	7.97 ,,
88 ,,	7.06 ,,
89 ,,	6.15 ,,
89.5 ,,	5.69 ,,

After the presence in butter-fat of considerable quantities of soluble acids had been fully proved, and no doubt could be entertained that our original conclusions were essentially correct, based though they were upon imperfect methods of investigation, Mr. Wanklyn ingeniously suggested, though it is difficult to see for what reason, that these soluble acids were not really present as such (of course combined with glycerine) in butter, but were only the product of the action of the alkali employed for saponification, upon the higher fatty acids. It is well known that the acids of the Acrylic series, $C_nH_{2n-2}O_2$, easily split up when acted upon by caustic alkalis, forming acetic acid and an acid containing two atoms of carbon less than the original acid; thus

$$-C_{18}H_{34}O_2 \text{ oleic acid} + 2 KOH = C_2H_3KO_2 \text{ (acetate)} \\ + C_{16}H_{31}KO_2 \text{ (palmitate)} + H_2; \text{ and there is good reason}$$

to believe that a similar acid might yield butyrate instead of acetate, under similar circumstances.

Mr. Wanklyn attributed the presence of butyric acid in the soap to the occurrence of such acids in the fat. As the difficulty of analysis of such substances as fat, and the separation of the fatty acids is exceedingly great, if not insurmountable, it is by no means easy to disprove or prove this theory (which of course does not reflect upon the practical applicability of our method). But the facts seem strongly to speak against its correctness. One would suppose, if such splitting up took place, it would do so by degrees, more in a hot solution than in a cold one, more with excess of alkali than with a small quantity. Yet the amount of fatty acids obtained is the same, whether the saponification take place in a boiling alcoholic solution or with aqueous alkali, or in the cold, as an interesting experiment by Dr. Dupré shows, who saponified in cold alcoholic solution, decomposed, and washed with large quantities of cold water. Against the theory further speaks the great specific gravity of butter-fat, as treated of at length in another chapter.

The decomposition of such acids, moreover, only takes place when fused caustic alkalies act upon the fatty acids, hydrogen being evolved; and there being, in the case of butter-fat, no great excess of alkali, we must entirely reject Mr. Wanklyn's otherwise ingenious theory.

At the same time it must be admitted that butyric acid does not exist in butter-fat as butyrate of glycerine. Mr. Bell has pointed out that if butter consisted simply of a mixture of glycerides, it could not be difficult to extract, by means of alcohol, the easily soluble butyrate, leaving the palmitate, stearate, and oleate for the most part undissolved. But, as the following quotation from Mr. Bell's paper will show, it appears that butter-fat contains the butyric acid intimately combined with the other fatty acids.

"A quantity amounting to 460 grammes was treated successively with twice its volume of alcohol of 92 per cent.; the alcoholic solution on evaporation gave 9 grammes of an oily fat which yielded 79.7 per cent. of fixed fatty acids, the remainder consisting of glycerine and the volatile acids.

"The butter-fat insoluble in alcohol was next treated with twice its volume of warm ether, and allowed to stand for several hours. A white crystalline fat separated, which was thrown on a filter and washed with a small quantity of ether. The ether was evaporated from both portions, and the specific gravity and fixed fatty acids determined. The crystalline fat, weighing 90 grammes, had a specific gravity of 909.55, and gave 89.50 per cent. of fixed fatty acids. The soluble fat, weighing 350 grammes, had a specific gravity of 912.35, and yielded 87.95 per cent. of fixed fatty acids.

"The portion soluble in ether was then treated with a mixture of alcohol and ether. Nearly one-half of the fat passed into solution. Both portions were freed from alcohol and ether. The soluble gave 86.50 per cent. of fixed fatty acids, and the insoluble 88.62 per cent.

"We then proceeded synthetically, by adding to a mixture of beef suet fat and dripping a given percentage of prepared butyrate of glycerin; 8 per cent. of the butyrin was dissolved in a fat of a specific gravity of 902.99 by the aid of heat. The specific gravity of the mixture at 100° Fahrenheit was 910.39. The mixture, when treated with alcohol, as in the preceding experiment, was almost completely freed from butyrin, as was shown by the residual fat giving a specific gravity of 903.44. The extractive by alcohol contained a little olein derived from the fat.

"The conclusion which may be drawn from these results is, that, contrary to the statement made by Berthelot and others, compounds of butyric and the other volatile acids present in butter with glycerine do not exist as simple glycerides, but

are in all probability present in a complex form, the radicals of the volatile fatty acids being combined with glycerin and the fixed fatty acids in the same molecule to form compound ethereal salts."

We have repeated these experiments, and entirely concur with the conclusions at which Mr. Bell arrived. Butter-fat is therefore to be regarded as glycerine, in which one portion of the hydrogen is substituted by the radicals of palmitic and oleic acid, and the other by the radicals of the soluble acids, amongst which, according to Dr. Dupré, butyric acid by far predominates. In other words, butter-fat is a mixed ether.

Such a theory would also explain the great constancy of the composition of butter. Of course, the pure mixed ether is never produced, but is always associated, to a greater or less extent, with other glycerides.

Stearic acid appears to be absent from butter-fat, whilst palmitic acid seems to be present in large quantities. Hence we may assume, for a moment, that butter-fat consists of such compound palmitic and oleic ethers. Both the di-palmitate, mono-butyrate and the di-oleate mono-butyrate would yield less insoluble acids than is found in practice, the former 80·2 and the latter 84·6 per cent. But a mixture of compound ethers such as would be obtained by substituting in the *tri*-palmitate or *tri*-oleate of glycerine one atom of hydrogen of the acid radicle by the radicle of butyric acid would very approximately yield proportions of insoluble and soluble fatty acids as are actually found. Whether butter-fat be or be not such an ether cannot at present be decided. Yet the question, from a scientific point of view, is highly interesting, and seems near the point of its solution.

CHAPTER VI.

SPECIFIC GRAVITY.

MR. BELL, of the Somerset House Laboratory, has added a very important factor to butter analysis, in pointing out that the specific gravity of butter-fat is greater than the density of other animal fats.

After the fact had been freely established that butter-fat contained a considerable proportion of glycerides, yielding butyric and other soluble acids, it could be surmised that, as the density of butyrim is greater than water, the gravity of butter-fat would be greater than that of other fats. Mr. Bell worked out this specific gravity test, the results being given in the following tables, which are copied from a paper presented to Parliament, and published in the *Pharmaceutical Journal*, July 22, 1876.

The specific gravity of the fats was taken at 100° F. in an ordinary specific gravity bottle, furnished with a sensitive thermometer, the mercurial portion of which extends nearly the whole length of the bottle.

Table I.—Results of Analyses of Animal Fats.

Description of sample.	Specific gravity at 100° Fahr.	Percentage of fixed fatty acids.
Mutton suet	902·83	95·86
Beef suet	903·72	95·91
Fine lard	903·84	96·20
Dripping (commercial) ...	904·56	94·67
Mutton dripping (genuine) ...	903·97	95·48

Table II.—Results of the Analysis of 117 Samples of Butter.

No.	Whence obtained.	Percentage of				Butter-fat.		
		Water.	Salt.	Curd.	Butter-fat.	Specific gravity at 100° Fahr.	Melting point, Fahrenheit.	Percentage of fixed fatty acids.
1	Surrey ...	4.15	—	—	—	913.49	Dg ^s . 86	—
2	„ ...	6.80	3.27	.80	89.13	913.09	88	—
3	„ ...	15.50	2.10	1.70	80.70	913.09	88	—
4	„ ...	11.40	.76	.77	87.07	912.28	90	—
5	„ ...	7.55	1.03	1.15	90.27	913.89	85	—
6	„ ...	12.70	.80	.86	85.64	912.79	86	—
7	Irish salt butter	11.67	2.20	.86	85.27	912.28	87.5	87.20
8	County Galway	11.79	3.39	.68	84.14	913.09	88.3	—
9	„	14.04	1.63	1.51	82.82	911.58	88.3	—
10	„	10.12	2.62	.70	86.56	912.99	88.2	—
11	„	4.91	1.54	.43	93.12	912.08	89	87.42
12	„	11.73	2.11	.47	85.69	912.99	89	—
13	„	11.83	1.14	.80	86.23	912.69	89	86.60
14	Devonshire ...	13.22	1.34	.68	84.76	912.69	87.8	—
15	Cornwall ...	16.99	2.65	1.36	79.00	912.39	88.7	—
16	Cumberland ...	12.26	4.52	.94	82.28	912.89	87.5	—
17	„ ...	11.92	4.22	1.52	82.34	912.39	87.5	—
18	„ ...	12.96	3.80	.36	82.88	912.99	88	—
19	„ ...	9.72	2.82	.28	87.18	911.98	88	—
20	„ ...	8.18	3.14	.92	87.76	912.69	87	—
21	„ ...	12.84	2.78	.98	83.40	912.69	87.5	—
22	Dorsetshire ...	16.85	2.77	.11	80.27	911.88	87.8	—
23	„ ...	16.37	3.22	.56	79.85	911.88	87.5	—
24	„ ...	17.06	2.13	.88	79.93	911.98	87.3	—
25	„ ...	17.03	2.25	.86	79.86	912.28	87.8	87.30
26	„ ...	18.37	1.63	.39	79.61	912.08	87.3	—
27	„ ...	13.24	1.25	.40	85.11	912.18	87.5	—
28	Cumberland ...	12.22	.61	.34	86.83	911.38	89.2	—
29	„ ...	13.02	.72	.61	85.65	911.28	90.2	—

Table II.—(continued.)

No.	Whence obtained.	Percentage of				Butter-fat.		
		Water.	Salt.	Curd.	Butter-fat.	Specific gravity at 100° Fahr.	Melting point, Fahrenheit.	Percentage of fixed fatty acids.
							Dgs.	
30	Cumberland ...	11.74	1.32	.42	86.52	911.68	90	—
31	„ ...	8.72	.58	.70	90.00	912.18	88.5	—
32	„ ...	9.55	4.17	.24	86.04	911.98	88.7	—
33	Suffolk ...	14.41	3.10	.64	81.85	912.39	89	86.87
34	„ ...	20.75	3.82	.61	74.82	911.58	92	87.80
35	„ ...	14.26	3.82	.22	81.70	912.89	88.5	86.45
36	„ ...	9.11	8.28	.40	82.21	912.79	88.5	86.00
37	„ ...	11.52	3.92	.41	84.15	913.89	87.5	85.50
38	„ ...	9.60	6.45	.82	83.13	912.28	89	—
39	Devonshire ...	14.36	2.66	1.46	81.52	912.99	88.5	—
40	„ ...	15.52	4.08	1.54	78.86	911.78	89	87.40
41	„ ...	17.56	2.98	1.14	78.32	912.39	89	—
42	„ ...	17.18	3.00	1.24	78.58	912.99	88.5	—
43	„ ...	16.28	3.32	1.56	78.84	912.79	88.5	—
44	„ ...	18.72	2.24	1.36	77.68	912.39	89	—
45	„ ...	16.42	2.80	1.60	79.18	912.23	88	86.87
46	„ ...	13.62	3.00	.60	82.78	910.78	90	88.00
47	Suffolk ...	13.14	5.74	2.96	78.16	913.97	88	—
48	CLondonderry	19.40	3.70	.56	76.34	912.96	89	—
49	„	13.70	2.30	1.86	82.14	912.28	90	—
50	„	15.94	2.40	2.68	78.98	911.06	91.5	—
51	„	18.52	4.84	2.16	74.48	911.91	90.5	—
52	„	14.90	6.04	1.50	77.56	911.88	90.5	—
53	„	14.98	3.74	1.14	80.14	910.97	91.5	—
54	Kent...	11.71	3.04	.76	84.49	913.14	88.5	—
55	„ ...	13.51	2.90	.70	82.89	913.09	88.5	—
56	„ ...	18.64	2.68	.79	77.89	910.50	93	88.60
57	„ ...	17.60	2.60	.98	78.82	910.63	93	—
58	Surrey ...	13.55	2.49	.80	83.16	910.93	92	88.35

Table II.—(continued.)

No.	Whence obtained.	Percentage of				Butter-fat.		
		Water.	Salt.	Curd.	Butter-fat.	Specific gravity at 100° Fahr.	Melting point, Fahrenheit.	Percentage of fixed fatty acids.
59	Surrey ...	14.16	—	—	—	912.23	Dgs. 89	—
60	County Cork	13.63	.44	.62	85.31	911.06	89.5	87.72
61	"	16.46	1.13	1.12	81.29	910.19	92.5	88.75
62	"	13.57	.65	.84	84.94	911.40	89	87.50
63	"	14.98	.68	.68	83.66	909.87	92.5	89.15
64	"	15.34	.40	.69	83.57	910.62	91	—
65	"	14.64	.46	.82	84.08	910.41	91.5	—
66	Carnarvonshire	11.41	3.03	.70	84.86	912.39	92	87.01
67	"	10.43	2.46	.57	86.54	911.48	89	—
68	"	13.79	2.96	1.26	81.99	910.63	93	88.32
69	"	11.05	7.71	.44	50.80	910.73	93	—
70	"	11.36	4.97	1.04	82.63	911.06	93	88.42
71	"	16.24	9.20	.40	84.16	911.34	93	88.12
72	Normandy ...	11.71	3.60	.95	73.74	911.45	90	—
73	Irish salt butter	16.89	8.56	1.23	73.32	911.48	89.5	—
74	Wiltshire ...	11.59	1.49	.44	86.48	912.01	90.5	86.96
75	" ...	13.21	1.74	.56	84.49	911.79	90.5	—
76	" ...	12.52	2.12	.79	84.57	911.46	90.5	87.35
77	" ...	11.99	2.23	.99	84.79	911.82	89	—
78	" ...	12.57	1.58	.89	84.96	911.48	90.5	87.65
79	Cumberland...	11.81	8.38	3.06	76.75	912.51	89	86.96
80	" ...	12.08	2.39	3.74	81.79	911.60	92	87.74
81	" ...	12.89	3.69	3.18	80.27	912.08	90	86.92
82	" ...	13.08	2.33	2.72	81.87	910.60	92	88.29
83	" ...	11.18	1.79	5.32	81.71	911.74	91.5	87.60
84	" ...	19.12	3.93	4.02	72.93	910.94	92.5	88.40
85	Cy. Monaghan	13.39	6.68	1.62	78.31	910.42	92.5	—
86	"	15.60	6.51	.54	77.35	910.14	92	88.90
87	"	13.59	15.08	1.36	69.97	909.47	93.5	—

Table II.—(continued.)

No.	Whence obtained.	Percentage of				Butter-fat.		
		Water.	Salt.	Curd.	Butter-fat.	Specific gravity at 100° Fahr.	Melting point, Fahrenheit.	Percentage of fixed fatty acids.
88	Cy. Monaghan	13.50	2.58	.55	83.37	911.04	Dgs. 91.5	—
89	"	14.55	5.86	1.31	78.28	910.30	93	—
90	"	12.43	3.55	.55	83.47	910.70	92	—
91	C Londonderry	11.81	2.85	.70	84.64	910.85	92	88.62
92	"	13.88	3.15	.75	82.22	911.47	90	87.66
93	"	14.34	3.31	.78	81.57	911.88	90.5	—
94	"	12.57	4.32	.51	82.60	910.65	92	88.74
95	"	13.56	2.29	.75	83.40	912.03	90.5	87.42
96	"	11.56	2.82	.47	85.15	911.79	90.5	88.05
97	Dorsetshire ...	13.92	2.13	.52	83.43	910.58	94	88.65
98	" ...	8.88	4.50	.50	86.12	910.85	92.5	88.46
99	" ...	12.55	2.22	1.35	83.88	912.20	91.5	—
100	" ...	12.81	1.78	.74	84.67	910.80	92.5	88.17
101	Staffordshire	10.61	1.11	.63	87.65	910.94	91.5	88.21
102	"	12.87	1.56	.76	84.81	912.44	89.5	87.14
103	"	12.84	1.67	.56	84.93	911.29	90	87.90
104	"	13.11	1.66	.46	84.77	911.78	91.5	—
105	"	10.93	1.25	.62	87.20	911.90	89	87.30
106	"	12.79	1.03	.66	85.52	910.11	93	—
107	County Sligo	12.36	3.24	.87	83.53	910.11	93	—
108	"	11.02	1.89	.87	86.22	911.76	91	—
109	"	14.61	3.86	.85	80.68	910.91	90.5	88.46
110	"	14.12	2.28	1.06	82.54	912.80	90	—
111	Cty. Galway ...	13.78	.90	.85	84.47	912.41	91.5	86.79
112	"	10.24	3.99	1.22	84.55	911.41	92.5	87.79
113	"	11.75	3.33	1.93	82.99	911.51	93	87.51
114	"	15.17	1.96	1.99	80.88	911.28	92.5	87.66
115	"	14.37	3.21	1.89	80.53	919.37	94.5	89.90
116	"	14.50	1.44	1.61	82.45	909.39	95	89.80
117	"	15.70	1.54	1.49	81.27	911.78	92	—

It will be seen from Table I. that the specific gravity of ordinary fats varies from 902·83 to 904·56, while the specific gravity of butter-fat as exhibited in Table II. rarely falls below 910, the usual range being from about 911 to 913. There is thus a material difference between the specific gravity of butter-fat and that of ordinary commercial animal fats, and it is obvious that this difference affords a satisfactory basis upon which to found an additional test for determining the purity of butter.

Dr. Dupré has shown that the specific gravity of fats may be much affected by previous treatment ; nevertheless, we consider it a very valuable test, and in cases where large numbers of butters are passing through the analyst's hands, may be used, together with the microscope examination, as a means of selecting those samples which shall be more fully examined.

We cannot help regretting that no mention is made in the tables of the microscopic appearances of these butters. Such a column would have been of use, we think, in accounting for the remarkably high percentage of water found in many of the samples ; as we have shown in the table given at page 19, we find that when water is present to an amount of more than 10 or 12 per cent., the sample usually appears to have been fused. This, and the fact that we have never yet met with a butter, *known to be pure*, with anything like so much water as many of Mr. Bell's samples evidently had, compels us to the belief that he placed too much faith in the agents which he employed to collect his samples.

Furthermore, we think the choice of the point 100° F. was a most unfortunate one. Even forgetting the fact, that most chemists have adopted the Centigrade scale, and that most scientific books give only degrees C., we think that 100° F. = 37·8° C. is far too low to be convenient. There

are but a very few fats which are liquid at that temperature, and the gravity of which can therefore be taken at that point. No lower point than 69.7° C., the melting point of stearin, should have been adopted, and 100° C. would have been far more in accordance with the obvious wants than 100° F. As the test is but of very recent origin, we hope that a new point may in future be adopted, for as yet it is not too late to mend.

The application of the well-known specific gravity bubbles to the measurement of the specific gravity of fats was first proposed by Mr. G. Wigner, F.C.S.,* who urges in favour of its adoption equal accuracy with other methods, and the small quantity needed, even as little as 200 grains being sufficient.

The following is the mode of procedure adopted :—

“Pour the liquid fat into a test tube of suitable size, put in the bubble, cool the fat until the bubble rises, then transfer the tube to a water bath, and raise the temperature of the water very slowly, until the bubble begins to sink, read the temperature at this time for comparison with genuine butter.”

The following results obtained by Mr. Wigner were given to show the bulbs likely to prove most suitable.

“Two bubbles were selected (the specific gravity of No. 1 was 899.7 , of No. 2, 895.7), both taken, of course, at 60° F. In a sample of butter, which at 100° F. had an ‘actual density’ of 913 , No. 1 bubble sank at 131° F.; No. 2, at 144° F. In another sample of fat, having an actual density of 911.3 , No. 1 bubble sank at 123° F., No. 2, at 135° F.”

Subsequently† Mr. Wigner pointed out an element of error which this process evidently contained, namely, the

* Note on the Specific Gravity of Fats. *Analyst*, No. 2, April, 1876.

† *Analyst*, No. 8, October, 1876.

alteration of the dimensions of the bulbs by the expansion of the enclosed air, caused by rise of temperature. It is plain that the gravity of the bubble, determined at 60° F., does not represent the actual gravity of the fat at the temperature at which the experiment is made, but requires a certain correction.

The mode of manipulation finally adopted was as follows :—

Into the test tubes containing the melted fat are fitted corks, bored with holes, through which are fitted pieces of glass rod, with rounded ends, long enough to dip a quarter of an inch or more below the surface of the fat. The bubbles are held by means of the glass rods, below the surface of the fat, and by this means surface adhesion, which would affect the results, is avoided.

The tubes being suitably supported are now immersed in water, at about 100° F., contained in a beaker; the beaker is itself immersed in another containing water at the same temperature. The whole arrangement is very slowly heated upon the said bath, until the bubbles are seen to detach themselves from the rods. They fall very slowly, but there is no difficulty in observing when the first line of separation is formed.

The following results obtained by Mr. Wigner are given as an illustration of the reliability of the method adopted :—

The clean melted butter-fat was weighed according to Dr. Muter's suggestion at 100° F. and 135° F.

Specific gravity at 100° F. compared with	
water at 60° F.	907.2
Corresponding to "actual density" at 100° F.	
compared with water at 100° F. ...	912.1
Specific gravity at 135° F. compared with	
water at 60° F.	895.2
Corresponding to "actual density" at 135° F.	
compared with water at 135° F. ...	906.7

A bubble, the specific gravity of which was 896, was tested in the fat and sank at 135° F. The indication given is therefore 896; as against a real specific gravity of 895.2 at 135° F., which corresponds to an error of 2° F. in temperature of specific gravity bottle at the time of taking the weight.

Butter-fat was then mixed with lard-fat in the melted state by successive additions of one-sixth of the latter by weight, so that No. 1 is pure lard, No. 2 five-sixths lard, and No. 7 pure butter.

These mixed fats were each tested with five bubbles of the following gravities at 60° F. :—

A and B	889.0
C and D	888.0
E	896.0

The following table was given to show the “actual densities” of these fats at 100° F., and the temperatures at which the bubbles were found by actual experiment to sink :—

Number.	Percentage of butter.	“Actual density.”	Temperature at which the bubbles sank.				
			Degrees Fahr.				
			A.	B.	C.	D.	E.
1	—	905.3	127	126	129	129	114
2	16	906.2	131	131	132	132	117
3	33	907.1	136	136	137	137	122
4	50	908.6	139	139	141	140	124
5	66	910.8	141	141	142	143	128
6	83	911.2	145	145	146	145	132
7	100	912.1	146	147	149	148	135

From these results it is seen that a sample of butter having an actual density of 911; the beads of specific gravity 889.

will sink at 145° F., and beads of 896· specific gravity will sink at 132° F. As a guide to the gravity it may be assumed that a difference of 1° F. in the sinking temperature indicates ·30 actual density, equal to about ·35 per cent. of insoluble fatty acids.

The application of that well-known and delicate instrument for the determination of specific gravities, Westphal's balance, to butter analysis, has been suggested by C. Estcourt (*Chemical News*, vol. xxxiv. No. 890). "The bulb of the balance is suspended in the test tube (1¼ in. by 5 in.) which contains the fat. This test tube is immersed in a metal tube containing paraffin (any other substance with a high boiling point will do), which is closed at the bottom. This tube is fastened securely by luting, etc. on to the lid of a small water-bath of suitable size, which has an outlet for steam, to which a glass tube can be attached and a tube at the side to indicate the quantity of water in the bath." These precautions and arrangements are necessary in order to avoid the condensation of steam on the beam of the balance.

When the temperature of the paraffin indicates 206° F., the weights on the balance are exactly adjusted, and the specific gravity is read off, when the temperature becomes stationary, which, in Mr. Estcourt's instrument, takes place at 208° F.

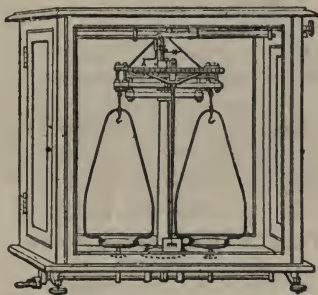
The following results were thus obtained by Mr. Estcourt:—

Beef fat	860·0	
Mutton fat	860·6	
Lard, home rendered...	862·8	
Butter M.	870·0	
Butter BB.	870·7	Calculated
Equal weights of mutton fat and butter	865·6	...	865·0			
Equal weights of beef and butter	...	865·7	...	865·8		
Equal weights of lard and butter	...	865·8	...	866·4		
Dutch butterine	865·2		

It will be observed that Mr. Estcourt takes the specific gravities at a temperature approaching as nearly as possible that of boiling water. He places, however, but little reliance upon the specific gravity test, for he advises, "as the best practical method of estimating fairly the percentage of adulteration, that after the gravity has been obtained, the fatty acid determination be made," especially in cases which may result in legal proceedings against the vendor.

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Appendix II.—List of Analytical Apparatus and Reagents, with prices.

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